

X-RAY CRYSTAL STRUCTURE ANALYSES
OF SOME PSEUDO-OCTAHEDRAL COMPLEXES OF
TERVALENT VANADIUM, CHROMIUM, MOLYBDENUM AND IRON

by

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Submitted in fulfilment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY

UNIVERSITY OF TASMANIA

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AUGUST, 1973.

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ABSTRACT

This thesis describes the results of three-dimensional X-ray crystal structure analyses of some coordination compounds of V(III), Cr(III), Fe(III) and Mo(III), specifically compounds containing octahedral complex ions, with a view to establishing important features of chemical interest.

A general outline is given of the process of crystal structure analysis with a detailed discussion of experimental techniques used in this research.

Two thiocyanates have been studied. For $K_3[Cr(NCS)_6] \cdot 4H_2O$ the trigonal unit cell dimensions are $a = 14.450$, $c = 9.625 \text{ \AA}$, and $z = 3$. These dimensions differ slightly from those reported by Zhdanov, Zvonkova and Glushkova. The analogous compound $K_3[Mo(NCS)_6] \cdot 4H_2O$ is also shown to be trigonal with $a = 14.510$, $c = 9.820 \text{ \AA}$, and $z = 3$. The two compounds are isomorphous. Weak intermediate layer lines have been observed in X-ray photographs of both compounds. This is possibly due to twinning, disorder or the presence of superlattice structures. For these reasons difficulties arose during this research which prevented complete determinations of structures. There is sufficient evidence, however, that both compounds contain $[M(NCS)_6]^{3-}$ ions.

Crystal and molecular structures of six compounds of the type $A_2^I [M^{III}Cl_5H_2O]$, with $A = K, Rb, NH_4$, or Cs ; $M = Fe$, or Mo ; have been determined. Unit cells, atomic parameters and bond lengths and angles are reported for each compound. Four of these adopt the orthorhombic $Pnma$ structure characterised by $[Rh(NH_3)_5Cl]Cl_2$: $K_2[MoCl_5H_2O]$, $(NH_4)_2[MoCl_5H_2O]$, $Rb_2[MoCl_5H_2O]$ and $Rb_2[FeCl_5H_2O]$. On the other hand, $Cs_2[MoCl_5H_2O]$ and $Cs_2[FeCl_5H_2O]$ are isomorphous with $Cs_2[RuCl_5H_2O]$, crystallizing with orthorhombic $Cmcm$ symmetry.

The structures of four vanadium(III) coordination compounds have been determined. The first of these, $\text{Cs}_2\text{VCl}_5 \cdot 4\text{H}_2\text{O}$ is monoclinic, space group C2/m , with $\underline{a} = 17.745$, $\underline{b} = 6.183$, $\underline{c} = 7.019 \text{ \AA}$, $\beta = 106.4^\circ$, and $\underline{z} = 2$. This structure comprises slightly distorted trans- $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ octahedra, Cs^+ and Cl^- ions and thus the compound should be formulated as $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$.

Work carried out in collaboration with Podmore has confirmed that the structure of $\text{Cs}_2\text{VBr}_5 \cdot 4\text{H}_2\text{O}$ is isomorphous with that of the chloro-salt.

The compound $\text{RbVCl}_4 \cdot 6\text{H}_2\text{O}$ crystallizes in the orthorhombic space group Cccm , with $\underline{a} = 10.291$, $\underline{b} = 15.566$, $\underline{c} = 8.319 \text{ \AA}$, and $\underline{z} = 4$. This compound contains slightly less distorted trans- $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ than $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$, together with Rb^+ and Cl^- ions and water molecules. The formula is thus $\text{Rb}[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$.

The halide $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$ is monoclinic, space group $\text{P2}_1/\text{c}$, with $\underline{a} = 6.408$, $\underline{b} = 6.550$, $\underline{c} = 12.300 \text{ \AA}$, $\beta = 96.15^\circ$, and $\underline{z} = 2$. This compound contains trans- $[\text{VBr}_2(\text{H}_2\text{O})_4]^+$ complex ions, bromide ions and water molecules, and thus should be written as $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$.

The structure of $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ has been elucidated from data taken from a twinned crystal. The crystals twin across the (010) plane to give a reciprocal lattice with apparent doubling of the \underline{c} -axis and with the glide plane of $\text{P2}_1/\text{c}$ suppressed to show apparent $\text{P2}_1/\text{m}$ symmetry. Cell dimensions are $\underline{a} = 6.430$, $\underline{b} = 6.439$, $\underline{c} = 11.901 \text{ \AA}$, $\beta = 98.8^\circ$. This compound is isomorphous with $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$.

Atomic parameters and bond lengths and angles are given for all five V(III) compounds. There is evidence of hydrogen bonding in each of the structures. The structures of these compounds are discussed comparatively.

ACKNOWLEDGEMENTS

I would like to thank Dr. P.W. Smith for his supervision of this research and for giving me the opportunity and encouragement to carry it out.

I am indebted to the late Dr. A.D. Wadsley of C.S.I.R.O. for starting me on the path of X-ray Crystallography and for advice in the initial stages of this research.

I would like to record special thanks to Mr. A.J. Finney of these laboratories for the extensive work he has put into writing the computer programs for X-ray crystallographic calculations used in this research and also for many helpful discussions on the progress of the structure determinations.

Computing facilities were provided by the University of Tasmania Computing Centre and by the Monash University Computing Centre.

Dr. P.G. Leverett and Dr. B.M. Gatehouse of the Chemistry Department, Monash University provided valuable assistance by allowing me to use their facilities on several occasions.

My thanks are due to Dr. R.S. Stoessiger and Mr. L.P. Podmore for some of the crystalline samples used, for collaboration in the powder photography concerned and for collaboration and discussion in some of the structure determinations. Likewise my thanks are due to Dr. H.P. Avey of the Tasmanian College of Advanced Education for fruitful discussions.

I wish to thank Mrs. B. Thomson and Mrs. H. Hen for preparation of the manuscript.

Lastly I would like to thank Professor H. Bloom in whose Department this research was undertaken, and particularly for his encouragement during the later stages of this work.

Chapter 1. X-Ray Crystal Structure Analysis

1.1. Introduction

This thesis describes the application of X-ray diffraction to the solution of crystal and molecular structures of a number of coordination compounds of trivalent, transition metal ions. Initially, interest centred on metal to ligand bonding problems encountered in thiocyanates of chromium and molybdenum. Later research followed structural questions brought to light by others in the Inorganic research group at the University of Tasmania. These dealt particularly with aquopentachloro complexes of Mo(III) and Fe(III) and several aquohalide complexes of V(III).

The purpose of this chapter is firstly to outline in a general fashion the process of X-ray crystal structure analysis. Then follows a discussion of the specific experimental techniques employed in the structural studies reported herein. The chapter concludes with a discussion of accuracy and precision of the experimental data and of the results of the structure determinations.

1.2. Crystal Structure Analysis¹⁻¹¹

1.2.1. X-ray diffraction

For the purpose of describing the diffraction of X-rays, a crystal may be considered as a distribution of electrons which is periodic in three dimensions.

X-rays have wavelengths of the order of the interatomic distances in crystals. Because of this the electrons surrounding the atomic nuclei in

a crystal diffract incident X-rays. Soon after the discovery of this phenomenon by von Laue and co-workers in 1912¹²⁻¹⁴, W.L. Bragg¹⁵ demonstrated that diffraction could be treated as reflection from planes in the crystal lattice. (Fig. 1.1).

Diffracted beams will only appear if the path lengths of rays reflected by planes of the same set differ by an integral number of wavelengths.

For this reinforcement to occur,

$$n\lambda = 2d \sin \theta \quad (\text{where } \lambda = \text{wavelength and} \\ n = \text{integer})$$

and this is known as the Bragg equation.

The regular arrangement of atoms or ions which gives rise to an electron distribution can be regarded as having been generated by the repetition of a fundamental unit called the unit cell. The unit cell can be characterised by three axial lengths, a, b and c along the x, y and z coordinate directions respectively, with the angles between the axes being α , β and γ as shown in Fig. 1.2.

It is convenient in crystallography to consider parallel lattice planes which have fractional intercepts on the three axes. The indices (h, k, l) which characterize each plane are called Miller indices.

Bragg also showed that the intensities of diffracted X-ray beams are proportional to the squares of complex quantities called structure factors. Each plane (hkl) of the unit cell has a structure factor:

$$F_{(hkl)} = \sum_{n=1}^N [f_n \exp 2\pi i(hx_n + ky_n + lz_n)]$$

where f_n is the atomic scattering factor of the n^{th} atom, x_n , y_n and z_n , are the positional coordinates of the n^{th} atom, expressed as fractions of the unit cell edges.

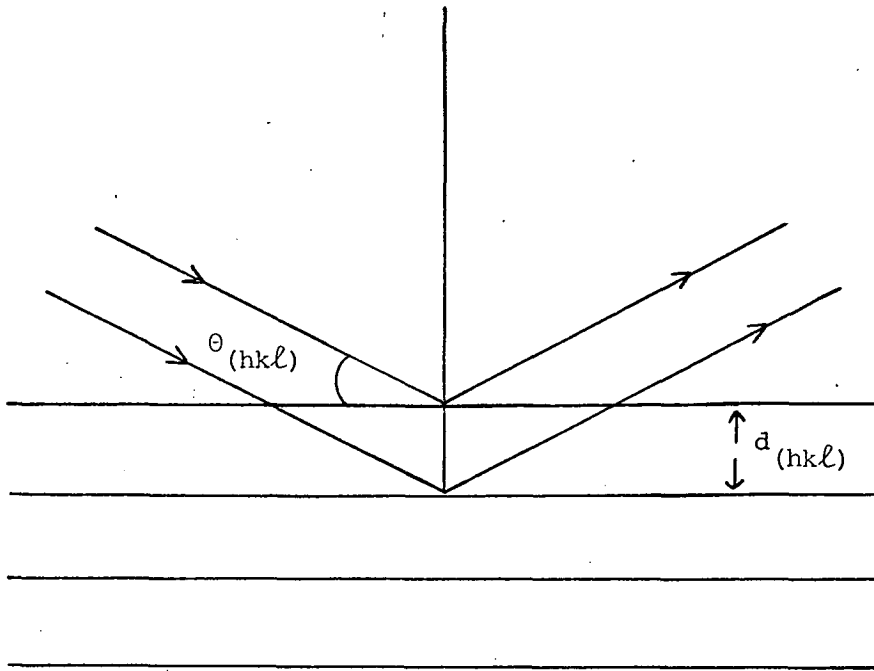


Fig. 1.1

Reflection of X-rays from planes in a crystal lattice

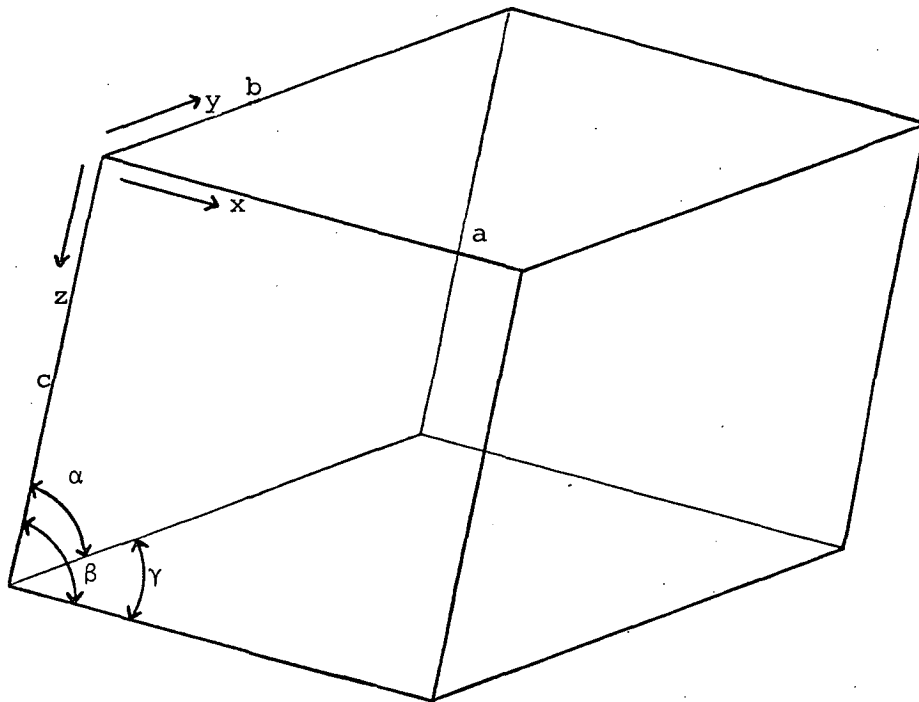


Fig. 1.2

The generalized unit cell

The modulus of the structure factor is given by:

$$|F_{(hkl)}| \propto \sqrt{I_{(hkl)}} \text{ where } I = \text{intensity of diffracted beam.}$$

This structure amplitude $|F_{(hkl)}|$ is defined as the ratio of the amplitude of the radiation scattered in the order (h, k, ℓ) by the contents of one unit cell to that scattered by a single electron under the same conditions².

The electron distribution in a unit cell can be expressed as a Fourier series:

$$\rho_{(xyz)} = \frac{1}{V} \sum_h \sum_k \sum_\ell [F_{(hkl)} \exp 2\pi i (hx + ky + \ell z)]$$

where ρ = electron density and V = unit cell volume.

Thus if the structure factors, $F_{(hkl)}$, are known together with their signs the electron density at any point in the unit cell can be determined and in principle, the structure can be solved. The structure factors are, however, complex quantities, having both amplitude and phase. Since only the amplitude can be obtained directly from the intensities, other methods must be used to determine the phase. This is the "phase problem" of crystal structure analysis.

There are several methods which can be used to help solve the phase determination problem. Of these the Patterson method, is one of the most widely used and was applied successfully in the crystal structure analyses described herein.

1.2.2. The Patterson Method

In 1934 Patterson^{16,17} suggested that while $F_{(hkl)}$ relates to the electron density distribution within the unit cell, $|F_{(hkl)}|^2$ which is obtained from the intensities, relates to the distribution of interatomic vectors. This can be expressed as a Fourier series:

$$\rho(uvw) = \frac{1}{V} \sum_h \sum_k \sum_{\ell=-\infty}^{+\infty} [|F_{(hkl)}|^2 \exp 2\pi i(hu + kv + \ell w)]$$

The Patterson map obtained from a plot of this function is a map of all interatomic vectors reduced to a common origin. Thus to every pair of atoms there is a specific peak in the Patterson map together with an origin peak representing the zero vector of each atom to itself, giving a total of $(n^2 - n)$ non-origin peaks for n atoms in the unit cell. It is sometimes possible to deduce the arrangement of atoms which gives rise to the vector peaks of the Patterson map by inspection. It is difficult however, to solve a Patterson for a structure containing many equal atoms because of problems associated with peak overlap and with the difficulty of identifying one peak from many similar sized peaks as being due to a particular atom-atom interaction.

This problem is simplified if there is a heavy atom or a small number of heavy atoms in the structure. These give rise to prominent vector peaks on the Patterson map and often make it possible to assign particular locations to the heavy atoms.

Within the Patterson map it is often convenient to consider particular concentrations of vector points referred to as Harker lines and planes¹⁸. These Harker concentrations of interatomic vectors arise from the interaction of atoms related by symmetry elements of the crystal space group. For example, the presence of a two-fold axis parallel to the

monoclinic b-axis in space group $P2_1/m$ gives rise to vector concentration in the Harker plane (uOw). In many cases, most of the interatomic vectors occur in these Harker lines or planes and this leads to a simplification of the process of phase determination.

1.2.3. Trial Structure and Refinement

Use of one or more of the methods of obtaining the phases of the structure factors results in a trial structure. This trial structure may represent all or only part of the structure, but it often enables the complete crystal structure to be found and refined.

For the trial structure, structure factors can be calculated. A comparison between observed and calculated structure factors can give some indication of the correctness of the model. This can be done by inspection, but it can be made quantitative by calculation of a residual index R , which is defined as:

$$R = \frac{\sum |\Delta F|}{\sum |F_o|} = \frac{\sum [|F_o| - |F_c|]}{\sum |F_o|}$$

where F_o = observed structure factor and F_c = calculated structure factor.

If the trial model has resulted in some reasonable correlation of observed and calculated structure factors, the phases of the calculated values can be assigned to the observed data and these used to calculate a Fourier (electron density) map of the unit cell.

Evaluation of this Fourier map may provide information about changes that need to be made to atomic positions and can provide an initial basis for structure refinement. This refinement process is severely limited by the fact that a Fourier series is infinite and that only a very finite

number of terms can be obtained from the X-ray data because these data are limited by the size and shape of the unit cell.

A much more versatile refinement process is the difference Fourier technique. The coefficients used in this type of Fourier series calculation are the difference between observed and calculated structure factors. The electron density expression becomes:

$$\rho_{(xyz)} = \frac{1}{V} \sum_h \sum_k \sum_\ell [\Delta F_{(hkl)} \exp 2\pi i (hx + ky + \ell z)]$$

The calculation results in an electron density map of the differences between observed and calculated electron densities and does not suffer from series termination effects. The structure can thus be refined to a much greater extent than by the ordinary Fourier technique. This is because the difference Fourier map gives direct evidence for any changes that need to be made to the atomic parameters of the original model.

The difference Fourier can be regarded as the difference between two Fourier syntheses calculated for observed (F_o) and calculated (F_c) structure factors respectively. The Fourier from F_o values would show peaks for real atom positions and that from F_c values would show peaks where atoms are postulated to be. Thus in a difference Fourier an atom which has been correctly placed should show up as background in the map. If the atom has been misplaced a hole (from F_c) will occur and a corrected peak (from F_o) will indicate where the atom should be. Small errors in atomic placement show up as a steep gradient between a hole and a peak and the trial atom position can be corrected by moving its location up the slope.

Having obtained a complete structural model and reached a degree of refinement using the difference Fourier technique, final refinement is usually carried out by the method of least squares. In this calculation

the quantity minimised is:

$$D = \sum_h \sum_k \sum_\ell w_{(hkl)} (|F_o| - |kF_c|)^2 \text{ (where } k \text{ is a scaling parameter)}$$

which represents the disagreement between the observed and calculated structure amplitudes. A weighting factor $w_{(hkl)}$, can be applied to each $(|F_o| - |kF_c|)$ according to its importance. The computation is arranged so that the assumed positional and thermal parameters are adjusted to give structure amplitudes of best agreement with the observed quantities. This method only works satisfactorily on a reasonably refined structural model, and cannot be used of itself for the initial solution of the structure.

1.2.4. Conclusion

A precise X-ray structure analysis gives a complete picture of the unit cell of a compound. The difficulty, however, lies in arriving at this precise analysis. As has been shown above (Section 1.2) it is not possible to proceed directly from the experimental data for the structure of a compound. It is often a complex and lengthy task to match structure factors from trial structures with those from observed diffraction effects. Arrival at suitable trial structures depends greatly on the extent of knowledge available and to some extent on computational facilities.

The X-ray diffraction technique also suffers from the limitations that it is often very difficult to find very light atoms like hydrogen, or to distinguish between atoms of neighbouring atomic numbers. In these cases, other techniques such as neutron diffraction can be used to solve these problems.

Despite these difficulties, X-ray analysis provides the best known technique for the solution of crystal and molecular structures of crystalline compounds. From these determinations bond lengths and angles can be calculated from the atomic parameters, as can intermolecular distances and spatial configurations. From atomic thermal parameters the thermal motions of individual or bonded atoms can be described.

1.3. Experimental Techniques

1.3.1. Crystal selection and mounting

The main aims in crystal selection are to choose crystals which possess uniform internal structure and which are of a proper shape and size. The ultimate test applied to crystals with respect to their internal structure is that the diffraction patterns consist of single, discrete diffraction spots capable of being indexed on a single lattice. It is often common for problems such as twinning of crystals to occur. In such cases it is usually difficult to isolate diffraction data from individual members of a twinned crystal but it is possible to do so. (See Section 6.3).

In determining a proper shape and size for crystals selected a number of factors have to be taken into account. The crystal should be smaller than the dimensions of the primary X-ray beam so that all the crystal is exposed to the same radiation intensity. For example, if the beam used has a diameter of approximately 0.5 mm the crystal chosen should be of smaller size. On the other hand the crystal should be large enough so as to provide an adequate amount of data over a reasonable exposure time. In particular, care has to be taken to select crystals of a uniform size, small enough to neglect corrections for absorption. (See section 1.5.1). The net result of these considerations usually requires the selection of crystals of dimensions less than 0.2 x 0.2 x 0.2 mm.

For reasonably stable compounds the crystals can be mounted on the ends of thin glass fibres and held in place by an adhesive such as shellac dissolved in alcohol. Crystals that are unstable in air or moisture have to be mounted differently. One technique is to coat the crystal with an inert material such as nujol and to seal it in a glass capillary tube. If inert coatings are inadequate an alternative mounting technique, may be to shake some crystals into capillaries drawn out of the side of a vacuum

reaction vessel and to seal off these capillaries under a dry inert atmosphere. This is a tedious process and usually has to be repeated many times before an appropriate single crystal in a suitable orientation is located in the tube.

Having selected a suitable crystal by one of the above methods the fibre or capillary is glued to the top of a goniometer head using an adhesive, such as shellac or plasticine.

1.3.2. Crystal Orientation

The goniometer head to which the mounted crystal is fixed is screwed into a rotating spindle of an X-ray camera. This camera is itself mounted on an X-ray generator. The crystal as mounted usually requires corrections to be made to the goniometer arcs to bring the rotation axis perpendicular to the X-ray beam. This can be done in several ways. One method which is used for a Weissenberg camera is as follows²⁰. (For a description of the Weissenberg technique see Section 1.3.3). Initially the goniometer head is oscillated through an angle of about 10° using unfiltered radiation and the resulting X-ray oscillation photograph is examined for misalignment of reciprocal lattice planes.

The goniometer head is orientated with the bottom arc parallel to the X-ray beam direction and oscillated between $5-10^\circ$ about this position. From such an oscillation photograph it is possible to identify the type of "pitch" and "roll" errors causing misorientation, and to simultaneously correct for both of these by applying correction angles, α, β to the bottom and top arc respectively. By measuring displacements at different values of 2θ several simultaneous equations of the form:

$$d/r = \sin 2\theta \sin \alpha + (1 - \cos 2\theta) \sin \beta$$

$$(d = \text{total displacement} = a + b)$$

a = roll displacement

b = pitch displacement

r = radius of the film).

can be set up and solved by least squares methods to give accurate values of α and β . Two successive applications of the procedure will bring the crystal into correct alignment. This method requires tedious calculations and in actual practice approximations are usually made in determining the corrections to be applied.

1.3.3. Weissenberg Technique²¹

A method commonly used to determine the space group and symmetry of a crystal as well as to obtain values for cell dimensions and intensity data is the Weissenberg equi-inclination technique.

This technique consists of isolating a single layer line, say ($h0l$) by placing an adjustable slotted screen about the goniometer head and between it and the film. The screen can be adjusted to isolate any one of the layer lines up the axis of rotation. The crystal is rotated and the film translated past the slit giving an expanded photograph of the particular layer line being examined. This photographic method permits the recording of a single layer as a two-dimensional array of diffraction spots.

As each layer line is selected by moving the slit, the camera is turned to an inclination angle which is related to the reciprocal lattice distance between the zero and upper level being considered. From Weissenberg photographs taken about the different crystal axes it is possible to determine the unit cell parameters, symmetry and possible space

groups for a crystal. It is often difficult, however, to visualize the reciprocal lattice directly on the Weissenberg photographs, particularly when axial traces may not be present and there are other systematic absences of spots to complicate matters.

To overcome this, the diffraction spots on any level can be reduced to a plot of the reciprocal lattice plane by the use of polar coordinate graph paper ~~polargraph paper~~. The r and θ coordinates of each spot can be measured by use of an apparatus described elsewhere⁵.

1.3.4. Intensity Data Collection

The selected crystal having been aligned and cell dimensions and symmetry determined from preliminary photographs, the intensities of reflections can be collected by taking equi-inclination Weissenberg photographs of as many reciprocal lattice planes as possible.

The main problems which arise are as follows:-

- (a) Radiation effects from scattering of X-rays by all objects in the beam.
- (b) Spectral impurity of the incident beam which give dark streaks through some diffraction spots.
- (c) Irregularity of spot size and shape brought about by changes in area of reflecting surface as the crystal rotates and by geometric factors.

Allowance can be made for the first two of these because they manifest themselves in such ways as darkening of strips of the film, as white radiation streaks passing through reflections and as the splitting of spots into K_{α_1} and K_{α_2} components. The third problem can often be overcome by integrating the intensity spot. An integrating device is used in conjunction with the film carriage to produce spots of reasonably

regular shape, usually square or rectangular^{22,23}. In many cases, however, preliminary non-integrated Weissenberg photographs show good spot size and shape. Since this requires less than half the recording time of integrated photography, non-integrated photographs are often used in such cases.

In order to extend the range of intensity data collection it is common to use 4-film packs to allow the more intense reflections to fall into a measurable range on the films. This photographic method of data collection²⁴ requires four pieces of film (5 x 7") to be packed into the camera and the whole exposed to reflections from a particular lattice row scanned by the Weissenberg technique. For non-integrated reflections it is usually found possible to collect data for the zero levels in about 40-60 hours, such that the strongest reflections can be measured on the fourth film in the pack. For each successive upper level film, collection time is usually increased by about two hours per photograph. In this way it is found that the measured intensities from various levels then fall onto approximately the same relative scale. This can be checked because layer scale factors obtained in the least-squares refinement stages should require only minor adjustments with respect to one another.

1.3.5. Measurement of Intensities²⁵⁻²⁷

The measurement of intensities can involve eye comparison of reflection spots with those on a linear scale in an arithmetic progression from 1 to 20, the process being carried out on a light box. One method of making a scale is to fix a lead screen on a goniometer head. In the centre of the screen a hole is cut of approximately the same dimensions as the spot shape. This hole is bathed in copper K_{α} radiation and the resulting spot recorded. Twenty such spots are recorded on adjacent parts of the X-ray film by moving the camera by a small amount after each exposure. The exposures are made at one second intervals from one to twenty seconds.

The reflections on a particular level are first indexed by sketching a reciprocal lattice grid on a tracing paper overlay and checking this against the polar plot of the reciprocal lattice for that level.

Each diffraction spot on the Weissenberg film is measured through the four films in the pack. With experience it is possible to measure about 200 spots per day without overtaxing the eye or introducing large errors in the measurements. There are, of course, many problems experienced in using this visual method of measurement. It appears to be a matter of experience to attain a reasonable degree of accuracy.

On upper level films it is very noticeable that expansion and contraction of spots leads to errors in estimation. Quite often it is possible to find an equivalent reflection on another part of the film that does not suffer from these effects. If such suitable reflections cannot be located it is usually found possible to correct for these effects by multiplying reflections by the ratio of length to a standard size, if the length of the spot varies by a large amount from this standard. This standard spot length is determined from zero-level photographs of each compound because this level usually is not subject to distortion of spot size. This intensity correction technique is an approximation of a formula derived by Phillips^{28,29} for extended reflections.

Another error can be introduced with the splitting of spots at high $\sin\theta$ into the K_{α_1} and K_{α_2} components. Care has to be taken to measure the intensities from both components and to sum these to give the overall spot intensity.

Problems of variable background due to radiation scattering effects or of spectral impurities present are automatically allowed for because the eye adjusts to background in the comparison between scale and spot. Because the eye has natural integrating properties, measurements carried out in this fashion often closely approximate to integrated intensities. This is

another reason why integration of spots is often not carried out, especially when preliminary investigations have shown that reflections present are of reasonably regular shapes and sizes.

The overall accuracy of the visual estimation can be as low as a deviation of 10% but it is suspected that for non-integrated data that after careful measurement and adjustment for other errors that an overall accuracy of approximately \pm 15% in the intensity (I) is more likely.

From the data collected in this way it is possible to calculate a film factor giving intensity relationships between successive films in the same pack³⁰. This enables the intensities of reflections to be assigned values relative to their intensities on the first film.

In most cases quite a number of possible reflections are not observed because their intensities are less than the minimum observable value. If sufficient reflections are observed to provide enough data for an accurate structure determination, it is not necessary to extend the data collection range to include the previously unobserved reflections.

For various reasons, such as extreme instability of a compound, it is often possible to only collect data about one crystallographic axis. Data collection about one axis to an angle of approximately 30° results in about 30% of the sphere of reflection being unexplored.

This omission of data does not prevent structure determination to a reasonable degree of accuracy but does give some uncertainty to the final parameters associated with the rotation axis.

1.4. Calculations^{31,32}

A major portion of the calculations involved in crystal structure determinations is usually carried out on a computer. A suite of X-ray crystallographic programs which can be used for this purpose are described in Appendix 1.

1.5. Accuracy in Structure Determinations

As well as determining the gross crystal structures of compounds, one of the main objects of X-ray structure analysis is to obtain bond lengths and bond angles between certain atoms in the crystal lattice. These parameters are derived from a set of atomic coordinates which are themselves dependent on the observed data, the structure amplitudes. Thus in determining the accuracy of bond lengths and angles, the errors in calculation of atomic parameters and in measurement of structure amplitudes must be taken into account.

The errors inherent in X-ray structure analysis are usually classified as random and systematic errors. Random errors result from a variety of causes which it is impossible to know or control and which give rise to the spread of the normal error curve and these will be discussed later. The other type of errors are those that affect measurements in a systematic way. The most prominent of these are discussed below.

1.5.1. Systematic Errors

Absorption^{1,3}

The absorption of X-rays by a crystal is a function of the crystal shape and the relation of this shape to the direct and diffracted X-ray beams. This results in differing absorption effects for each reflection measured and corrections can be extremely tedious.

To correct the observed intensity of a reflection, I_0 for linear absorption the following expression can be used:

$$I = I_0 e^{-\mu t} \quad \text{where } t = \text{thickness, and } \mu = \text{linear absorption coefficient.}$$

μ can be calculated from:

$$\mu = G \sum_p \left(\frac{\mu}{p} \right) \quad \text{where } G = \text{density of the crystal}$$

$\left(\frac{\mu}{p} \right) = \text{mass absorption coefficient}$
 $p_A = \text{fraction by weight of element}$
 A in compound ABC...

Absorption corrections can often be neglected if crystals of suitable dimensions are chosen. The omission of these absorption corrections sometimes leads to smaller values of isotropic thermal parameters after the structure refinement. This gives a small reduction in accuracy but not necessarily in precision.

Extinction^{1,2}

The extinction effect results in an attenuation of the primary X-ray beam when the crystal is in a diffracting position and thus reduces the intensity of the diffracted beam. There are two forms of extinction.

(a) Primary Extinction

This occurs when the intensity of a beam is reduced by interference as it passes through a crystal. Most crystals are made up of mosaic blocks which are usually small enough so that primary extinction can be neglected.

(b) Secondary Extinction

For some reflections an appreciable amount of incident radiation is reflected by the first planes encountered by the X-ray beam. The deeper planes thus receive less incident intensity of radiation and reflect less powerfully than should be the case. It follows that this effect could be more pronounced for reflections of low $\sin\theta/\lambda$. Corrections for secondary extinction are not generally made because of their complexity. Towards

the end of structure refinement it is often common practice to examine reflections of $\sin\theta/\lambda < 0.2$ and to reject these from the final refinement if $F_{\text{calc}}/F_{\text{obs}}$ is substantially greater than the residual factor, R.

Scattering factors

Each atom in a structure has a certain X-ray scattering power which is a function of the atom type and $(\sin\theta)/\lambda$. The variation of the scattering powers of various atoms with $(\sin\theta)/\lambda$ is used for calculating structure amplitudes in the structure determination process. When the wavelength of the incident radiation lies near the absorption edge of a scattering atom, anomalous dispersion may occur. For these cases a correction to the scattering factors can be calculated by:

$$f_o^{\text{anom}} = f_o + \Delta f' + i\Delta f'' \quad \text{where } f_o \text{ is the normal}$$

scattering factor, $\Delta f'$ is a real correction term and $\Delta f''$ is the imaginary component. An approximation may be made to give:

$$f^{\text{anom}} = f + \Delta f'$$

In practice the scattering curves are often corrected for the real part of the anomalous dispersion and the imaginary part neglected in the centrosymmetric case. This is because it is usually small with respect to $\Delta f'$ and much more difficult to calculate. It is probable that any errors due to anomalous scattering would be very small in comparison, to say, absorption, and in fact refinement using scattering factors corrected for anomalous scattering often shows no appreciable difference from refinement without such correction.

Temperature factors

Temperature has the effect of spreading the electrons of an atom over a larger volume and this has an effect on the scattering factors of an atom.

In the simpler case of isotropic temperature correction the scattering factor can be modified by:

$$f = f_o e^{- (B \sin^2 \theta) / \lambda^2}$$

where B is called the temperature coefficient,

and $B = 8\pi^2 \overline{u^2}$ where $\overline{u^2}$ is the mean square amplitude of oscillation of the atoms from their mean position.

Anisotropic temperature corrections may also be allowed for and take the form of a more complex expression.

$$f = f_o e^{- (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{23}kl + b_{31}lh)}$$

The effect of using anisotropic temperature factors in least square refinement of a crystal structure, will invariably lower the value of R compared to that obtained from isotropic temperature factors. This does not of itself justify their use, particularly when there are systematic errors present, such as absorption which have not been corrected for.

Hamilton has proposed a test to identify meaningful changes in R produced when the structural model is changed³³. Suppose the R factor $R(1)$, using isotropic thermal ~~parameters~~ ^{parameters} drops to $R(2)$ after the introduction of anisotropic thermal parameters and further least squares refinement. The ratio $R(1)/R(2)$ can then be compared at given levels of significance (α) using Hamilton's tabulated values for the dimensions and degrees of freedom for a particular case. A significance level of 1% is commonly used for film data and this entails a risk of 1 in 100 of accepting as a

significant model improvement one which is actually not.

1.5.2. Random Errors

These physical factors which affect intensities can be corrected for either in the data reduction or least-squares refinement stages. The corrections required for geometrical factors affecting intensities are discussed in Appendix 1. What cannot be allowed for are errors which arise from equipment and its use. Precautions are taken to avoid gross sources of such undetected systematic errors but their presence must be kept in mind. It is possible therefore that the estimated standard deviations which take into account random errors, are often much smaller than errors not corrected for or not allowed for.

Errors in atomic parameters are due to³⁴:

- (a) Experimental errors in $|F_{\text{obs}}|$'s,
- (b) Imperfections of the molecular model used for the F_{calc} 's
- (c) Errors in unit cell size,
- (d) Computational approximation errors.

Standard deviations in atomic parameters account for the standard deviations calculated by the least-squares program and for the errors in the positions of the heavy atoms due to uncertainties in the weighting scheme. This estimation of standard deviations allows for (a) above. It also roughly allows for corrections to (b) except that it treats the latter as random errors when they are really systematic. This approximation can be checked against final difference Fourier maps where these should show no strong features attributable to the calculated model.

Thus the estimated standard deviations are calculated presuming a correct model and are then a measure of the consistency of the data set.

The accuracy of molecular parameters derived from atomic coordinates depends on the accuracy of these coordinates and on the accuracy of determination of unit cell dimensions. The order of accuracy of these cell dimensions required to match that of the coordinate determination is approximately one part in a thousand. This limit of accuracy would correspond to an error of less than 0.003 \AA in a bond length of 2.000 \AA . Measurements from single crystal photographs usually give cell lengths to about 1% and angles with errors of about $\frac{1}{2}^\circ$ ³⁵. For unit cells commonly encountered these limits of error are greater than one part in a thousand.

Accurate unit cell dimensions can be calculated from X-ray powder data.

The d spacings can be measured reasonably accurately from these powder data particularly when use is made of internal calibrants, such as sodium chloride or silicon metal³⁶. The unit-cell parameters can be refined by the least squares method by solving the overdetermined system of linear equations obtained by indexing the powder patterns.

Using this technique unit cell dimensions can be calculated with an accuracy of better than 0.1% and this provides a reasonable match with the accuracy of molecular parameters.

Chapter 2. Hexathiocyanates of Chromium(III) and Molybdenum(III)

2.1. Introduction

A wide range of studies has been carried out on the structures of complex compounds, where the rules of close packing of spherical groups often cannot be used to predict and explain the structures of such compounds. The presence of non-spherical groups in the form of, for example, thiocyanates and cyanides requires a different approach to structural problems. This has been attempted, for instance, by Zhdanov and Zvonkova in their study of simple and complex thiocyanates³⁸. For simple thiocyanate compounds they deduced that the fundamental pattern of the structure does not basically depend on the symmetry of the structural components of the crystal but, rather, on the nature of the chemical bond. Ionic bonding between the cation and the complex anion, and the formation of hydrogen bonds, both were used to explain structural modifications in these compounds.

For complex metallic thiocyanates Zhdanov and Zvonkova³⁸ have attempted to systematize the available structural information and use their conclusions to predict structures for most tetra- and hexa-thiocyanates. In some cases hydrogen bonding between water molecules and the N atom of the SCN^- group stabilizes the crystal, e.g., $\text{K}_2[\text{Cd}(\text{SCN})_4] \cdot 2\text{H}_2\text{O}$ ^{39,40} and in others the water molecules merely occupy vacancies in the crystal lattice, and only minimal decrease in stability is brought about by the removal of water molecules, as for instance in $\text{K}_2[\text{Co}(\text{NCS})_4] \cdot 4\text{H}_2\text{O}$ ³⁸.

Zhdanov and Zvonkova have also predicted that compounds of the type A_nB [Where $\text{B} = \text{M}(\text{NCS})_6^{n-}$] will have stratified lattices, consisting of layers of octahedral complex ions and cations. They have applied this theory to $\text{K}_3[\text{Cr}(\text{CNS})_6] \cdot 4\text{H}_2\text{O}$ and $\text{K}_4[\text{Ni}(\text{CNS})_6] \cdot 4\text{H}_2\text{O}$ ⁴¹ on the basis of these compounds having the same space group as $\text{K}_2[\text{Pt}(\text{SCN})_6]$, the structure of which has been reported by Hendriks and Merwin⁴². The X-ray structural evidence they

produce is, however, inconclusive.

The X-ray structure analysis of $K_3[Cr(CNS)_6] \cdot 4H_2O$ and of the analogous molybdenum compound, $K_3[Mo(CNS)_6] \cdot 4H_2O$ was the starting point of the research work reported in this thesis. There are several aspects of interest which arise in the structural study of these two compounds.

- (1) Coordination number of the central metal;
- (2) Attachment of the thiocyanate group;
- (3) The role of the water molecules;
- (4) The symmetry of the complex ions.

The formation of compounds, such as $K_3[Mo(CNS)_6] \cdot H_2O \cdot CH_3COOH$ and the experimental loss of three water molecules from the tetrahydrate $(NH_4)_3[Mo(CNS)_6] \cdot 4H_2O$ suggested to Maas and Sand^{43,44}, Pauling⁴⁵ and others that Mo(III) has a coordination number of seven in these type of compounds. More recently, however, Lewis, Nyholm and Smith^{46,47} have shown that $K_3[Mo(CNS)_6] \cdot 4H_2O$ loses four water molecules on dehydration, and furthermore that magnetic measurements suggest six coordination for Mo(III) in this compound. It is reasonable to expect, therefore, that other similar compounds should exhibit this six-fold coordination of the central metal ion.

Arhland, Chatt and Davies⁴⁸ proposed a division of elements, which can act as acceptors, into two groups on the basis of their affinity for coordinating with either the first or second element from each of three groups of ligand atoms in the periodic table. Class (a), being those which complex most strongly with the first elements, namely nitrogen, oxygen and phosphorus, while class (b) consist of those which form most stable complexes with the second or subsequent ligand atom.

The borderline between class (a) and class (b) acceptors falls around chromium and molybdenum in the transition metals and a convenient ligand

which can be used to decide into which class these elements belong is the thiocyanate ion⁴⁹. Pepinsky has shown from X-ray crystal structure studies that chromium is bonded to the nitrogen end of the thiocyanate group in such compounds as ammonium reineckate $\text{NH}_4[\text{Cr}(\text{NCS})_4 \cdot (\text{NH}_3)_2] \cdot \text{H}_2\text{O}$ ⁵⁰⁻⁵², and pyridinium reineckate⁵³.

On the basis of infrared studies, Lewis, Nyholm and Smith⁴⁶ have proposed molybdenum to nitrogen bonding in the compound $\text{K}_3[\text{Mo}(\text{CNS})_6] \cdot 4\text{H}_2\text{O}$ which has been shown by optical crystallography to be isomorphous with $\text{K}_3[\text{Cr}(\text{CNS})_6] \cdot 4\text{H}_2\text{O}$. This is contrary to an incomplete X-ray structural study of $\text{K}_3[\text{Cr}(\text{SCN})_6] \cdot 4\text{H}_2\text{O}$ in which Zhdanov et al⁴¹ report sulphur bonding to chromium in the $[\text{Cr}(\text{SCN})_6]^{3-}$ complex ion.

Lewis, Nyholm and Smith⁴⁶ also proved that it was possible to remove the four molecules of water from $\text{K}_3[\text{Mo}(\text{CNS})_6] \cdot 4\text{H}_2\text{O}$ although this was accompanied by decomposition of the product even in the absence of oxygen. The original compound is much more stable although it will decompose over a period of days on exposure to air under normal conditions. The same workers found, however, that the compound $(\text{NH}_4)_3[\text{Mo}(\text{CNS})_6] \cdot 4\text{H}_2\text{O}$ lost only three molecules of water under vacuum dehydration and the related compounds $(\text{NH}_4)_3[\text{Mo}(\text{CNS})_6] \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_3[\text{Mo}(\text{CNS})_6] \cdot \text{HCl} \cdot \text{H}_2\text{O}$ retained the water molecule under the same conditions. In these cases the water molecule remaining after dehydration is presumably held in the structure by strong hydrogen bonding with the ammonium cation, and this bonding has a strong stabilizing effect on the molecule.

It has been assumed that the bonding in the complex ion $[\text{M}(\text{NCS})_6]^{3-}$ is basically octahedral in nature⁵⁴⁻⁵⁸.

The six-fold coordination of the metal ion discussed above supports this assumption and as far as the M-N bonding is concerned this is no doubt correct. If the metal to thiocyanate bonding is completely linear the overall symmetry of the complex ion would remain octahedral, but if there is

some angular bonding character $M \begin{smallmatrix} \diagup \\ N=C=S \end{smallmatrix}$, as has been suggested by Lewis, Nyholm and Smith⁴⁶ then quite appreciable distortion from octahedral symmetry will take place.

To simplify the following account it is proposed first to outline in detail the crystal structure analysis as applied to $K_3[Cr(CNS)_6] \cdot 4H_2O$. Then reference is made to similar studies carried out on the analogous molybdenum compound.

2.2. Experimental : $K_3[Cr(CNS)_6] \cdot 4H_2O$

2.2.1. Preparation - Crystal Selection

The compound was prepared by the method of Maas and Sand⁴³. Dark red hexagonal plate shaped crystals were obtained after recrystallization from water. To obtain regular shaped single crystals it was found necessary to filter the crystals from solution before the compound formed a crust on the surface. The crystals are quite stable in air over long periods of time, and suitable specimens for single crystal X-ray studies were separated from the sample. Several of these crystals were glued to thin glass fibres with shellac, and oriented so that data could be collected around both the a and c axes of the trigonal cell.

2.2.2. Initial Data Collection

X-ray powder data were collected on a Guinier-Hagg camera using KCl as an internal calibrant. For single crystal work a Weissenberg camera was used. Oscillation photographs taken about the c-axis showed very weak intermediate layer lines between a strong set of layer lines (Fig. 2.1). Photographs taken about the a-axis showed signs of similar intermediate weak layer lines (Fig. 2.1). Attempts to index the powder data using the unit cell derived from the strong layer line oscillation and Weissenberg photographs proved only partially successful, there being several lines which could not be indexed. Doubling of the c-axis was more successful and it was



Fig. 2.1 Oscillation Photograph \underline{a} -axis rotation $\text{K}_3[\text{Cr}(\text{CNS})_6] \cdot 4\text{H}_2\text{O}$

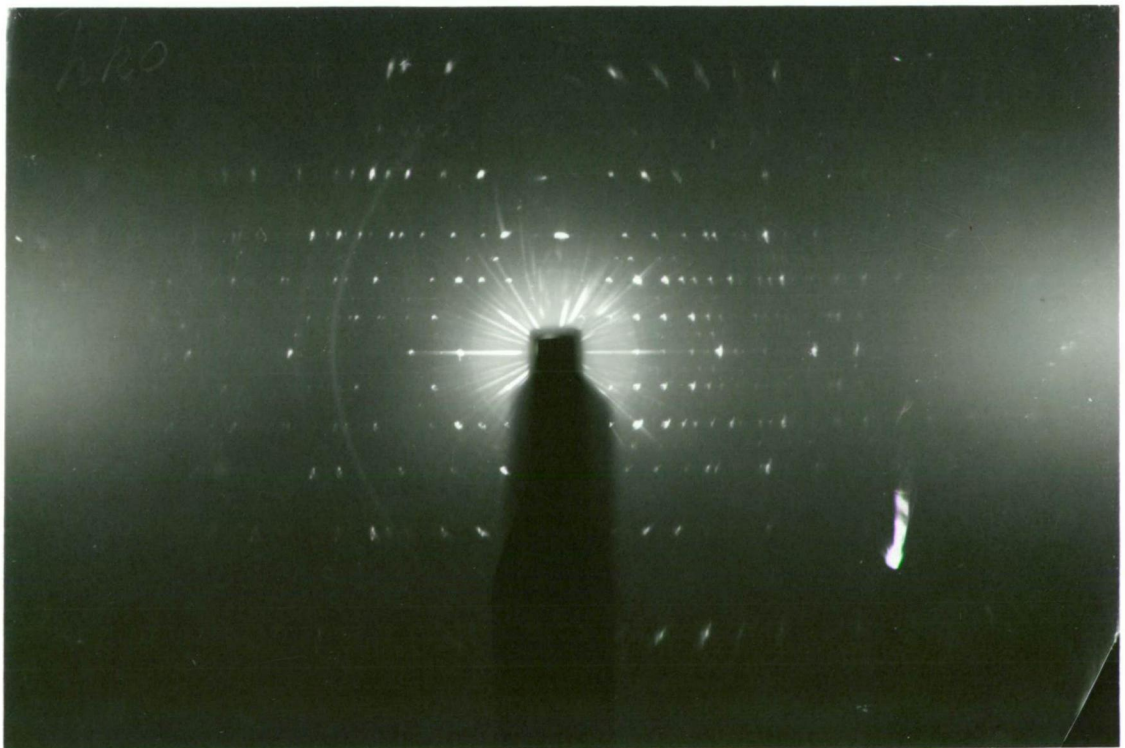


Fig. 2.2 Oscillation Photograph \underline{c} -axis rotation $\text{K}_3[\text{Cr}(\text{CNS})_6] \cdot 4\text{H}_2\text{O}$

found possible to index all but one or two very weak lines and one strong line. By doubling of all axes all the powder lines could be indexed, but this is probably to be expected anyway as the unit cell becomes very large.

To remove any doubts on the reliability of the powder data the measurements were repeated on several different samples using both KCl and Si as internal calibrants, and the data were checked against duplicate data obtained from a Philips powder diffractometer at different 2θ angles.

Unfortunately a computer program to refine the cell parameters by least squares methods on the powder data was not available for trigonal symmetry. The calculations were carried out manually and the final observed versus calculated $\sin^2\theta$ values are shown in Table 2.1 for both the large and small cells. The unit cell dimensions are shown later in Table 2.2 for convenience of comparative presentation.

The small cell corresponds to the spacings of the strong layer lines about both the a and c axes. It was thought that the weak layer lines and consequently the larger cell could be due to a number of possibilities. There could be twinning, disorder or superlattice problems.

At this stage the prospect of computing in the large cell presented local problems and it was not evident until later that great difficulties would also be encountered for the small cell as well. It was decided to collect three dimensional X-ray intensity data for both the weak and strong layer lines, and to attempt to solve the structure from the data for the small cell. It was hoped then to be able to explain the doubling effects, and to possibly carry out some calculations on the large cell. Problems had been encountered with twinning and trial Weissenberg data on some crystals showed this in the form of doubled reflections. It was possible, however, to obtain apparent single crystals by careful recrystallization and by selecting very small crystals for mounting. There still remained the possibility that the crystals used for intensity data collection were twinned

TABLE 2.1

X-Ray Powder Data : $K_3[Cr(CNS)_6] \cdot 4H_2O$ Cu K_α radiation : $\sin^2 \theta \times 10^4$

(Estimated intensities : s = strong, m = medium, w = weak, b = broad)

$\sin^2 \theta_{obs}$	Estimated Intensity	Small Cell		Large Cell	
		$\sin^2 \theta_{calc}$	Index	$\sin^2 \theta_{calc}$	Index
101.8	s	101.9	1 0 1	101.8	2 0 2
176.9	w	177.7	1 1 1	177.1	2 2 2
180.2	w	-	-	182.1	2 0 3
216.1	wb	215.6	2 0 1	213.7	4 1 1
329.9	m	329.3	2 1 1	327.7	4 2 2
334.6	w	-	-	333.8	6 0 0
364.5	w	-	-	364.3	4 3 1
369.7	w	369.7	1 1 2	370.3	2 2 4
401.0	vw	-	-	398.0	6 0 2
				401.5	0 0 5
405.4	m	405.1	3 0 1	404.6	6 1 0
407.7	m	407.6	2 0 2	408.0	4 2 3
414.4	vw	-	-	412.4	4 3 2
455.0	m	454.8	2 2 0	454.6	4 1 4
462.3	s	-	-	461.1	5 3 0
516.0	m	518.8	2 2 1	514.4	2 2 5
				515.9	4 4 0
523.8	m	521.3	2 1 2	523.8	3 1 5
				525.3	5 3 2
591.2	s	-	-	590.1	5 4 1
				590.8	6 0 4
604.9	w	606.4	4 0 0	605.2	4 3 4
				605.6	5 3 3
				606.4	4 3 4

TABLE 2.1 (Cont.)

676.3	vw	-	-	680.9	7 1 3
705.5	s	-	-	703.0	8 1 1 }
				705.8	5 5 0 }
711.9	m	710.8	2 2 2	708.7	4 4 0 }
				709.9	4 0 6 }
718.7	s	720.1	3 2 0	718.1	5 3 4 }
				718.5	5 4 3 }
741.5	vw	-	-	743.4	7 3 0
783.4	vw	784.1	3 2 1	779.4	6 4 2
788.8	vw	-	-	786.9	7 0 0 }
				790.4	8 2 0 }
796.2	vw	795.9	4 1 0	796.2	1 0 7

about the c axis in such a way as to superimpose reflections from two twins on the one film to give the appearance of reflections from a single crystal.

2.2.3. Intensity Data Collection

Strong layer line data

Integrated intensity data for hkn ($n = 0-5$) and for $nk\ell$ ($n = 0-5$) were recorded photographically by the Weissenberg equi-inclination technique using Cu K_α radiation and 4-film packs. The exposure times being of the order of 50-60 hours per film. Ilford Industrial G film was used. Developing time was 7 minutes at 25°C , fixing time 10 minutes at 25°C .

The data were collected from two small crystals, each of approximately the same dimensions in the form of small hexagonal plates mounted about the two different axes. The intensities were measured visually against a standard linear scale and the data put on a common scale by comparison of equivalent spots from the two different orientations.

The intensity data were corrected for Lorentz and polarisation effects but not for absorption or extinction. The Weissenberg photographs taken along $[001]$ showed trigonal symmetry, the repeat unit being 120° . For the small cell there were no systematic absences thus allowing a choice of space groups P_3 , $P_3\bar{1}$, $P_3\bar{2}$, $P_3\bar{1}2$, $P_3\bar{2}1$, $P_3\bar{1}2$ or $P_3\bar{2}1$.

Weak layer line data

Attempts to collect integrated data from the weak layer lines failed because of the length of exposure time required. For non-integrated data collected for four weak layer lines along the c -axis, exposure times of approximately 100 hours were required to obtain a fair spread of observed reflections. The intensities of 157 such reflections were measured by visual comparison against a standard scale.

Polar plots of these reflections revealed a very interesting phenomenon. The reflections obtained could only belong to a large cell with $a = 28.90$, $c = 19.25 \text{ \AA}$, and $z = 24$ and had indices with h and k values corresponding only with weak layer lines about the a -axis. The absence pattern for the large cell taking into account both strong and weak reflections is thus for $hkl : h+l = 2n+1$, a systematic absence not characteristic of any trigonal space group. This would appear to suggest that the strong data corresponding to the small cell should give a structure which is the average one for all cells with the weak reflections being possibly due to a superlattice structure.

2.2.4. Calculations

At the time this structure analysis was being carried out the suite of crystallographic computer programs in ALGOL as described in Appendix 1 was not available. The programs used were a version of the Wheatley⁵⁹ series in machine-code obtained from the late Dr. A.D. Wadsley of C.S.I.R.O. These programs were adapted for use on the Elliott 503 computer available to our laboratories, and their use suffered from the following severe limitations.

- (1) The least-squares program could not handle the refinement of trigonal symmetry with positions of the type $(x, 2x, z)$.
- (2) The Fourier program was not capable of calculating in trigonal symmetry, and even if it had been, the time taken to compute even a few sections would have been very long, with the need to incorporate about 1200 reflections in the calculation.
- (3) The computational time was extremely slow. A structure factors calculation on 300 reflections took approximately 1 hour and this without any refinement cycles. To calculate a Fourier of ten sections for the above data took a total of at least three hours. This time factor was later speeded up considerably but still compared unfavourably with the

Algol program suite as discussed in Appendix 1.

What was eventually done was to consider the trigonal unit cell as if it were a special case of triclinic. An examination of space group $P\bar{1}$ shows that the general and special positions available are sufficient to accommodate all the positions of the trigonal space groups, albeit with a diminished symmetry relationship in most cases.

It is possible, of course, to compute structure factors in triclinic symmetry by using a structural model derived from the trigonal space group. Problems arise, however, when attempts were made to refine coordinates and temperature factors by the method of least squares. In triclinic symmetry a six-fold atom position of the trigonal space group becomes 3 two-fold positions. Attempts at refinement shifted the coordinates of these positions independently of one another, with the result that the trigonal six-fold symmetry, initially superimposed, was lost. This required an evaluation of atomic coordinates after each attempt at refinement, followed by a manual calculation to return the coordinates to the trigonal symmetry before proceeding with the next stage of refinement.

Several attempts were made to get this system working, and although there was a slight reduction in the R factor, it was found difficult to refine the structure by significant amounts.

Attention was then turned to refinement by Fourier methods. Again the computer programs available precluded direct computation in trigonal symmetry and the process was carried out in the lower triclinic symmetry. This method of calculation was the basis of the attempts at structure determination and refinement described in the next section.

2.3. Discussion

During the course of this X-ray analysis the crystal structure of a similar compound $K_3[Mo(NCS)_6] \cdot H_2O \cdot CH_3COOH$ was reported by Knox and Eriks⁶⁰. Some crystallographic data from their study are shown in Table 2.2 in comparison with data from this present work. Knox and Eriks show that the Mo atom is octahedrally coordinated to the N end of the thiocyanate group, with the angle between adjacent Mo-N bonds being distorted away from the expected 90° of a regular octahedron. In the structure each potassium ion is surrounded by six sulphur atoms in a trigonal prism. In half the prisms a disordered potassium ion is replaced half the time by a water molecule; this causes the prism to expand, distorting the octahedron so that four Mo-NC angles deviate from linearity. Six sulphur prisms form a cavity in which the acetic acid molecule is located and bonded by a H-bond to the water molecule.

While this structure determination removed some of the reasons for continuing work on $K_3[Cr(CNS)_6] \cdot 4H_2O$ and $K_3[Mo(CNS)_6] \cdot 4H_2O$ the structure analyses had reached a stage where some interesting problems had been encountered. There were signs of twinning, disorder and superlattices in the trigonal cells of both compounds. The solution of these problems and confirmation of the metal to nitrogen bonding in the complex ions provided good reasons for continuing with this work.

The first and most logical step in determining the structure of $K_3[Cr(CNS)_6] \cdot 4H_2O$ was to try the Zhdanov, Zvonkova and Glushkova⁴¹ model. These authors had chosen the D_{3d} symmetry of space group $P\bar{3}m1$, but for reasons discussed above the calculations reported in this thesis were carried out in space group $P\bar{3}$ simulated in triclinic symmetry.

A structure factor calculation based on this Zhdanov model, however, showed very little relationship between observed and calculated data

TABLE 2.2

Crystallographic Data

	$K_3[Cr(NCS)_6] \cdot 4H_2O$ (This work)		$K_3[Cr(SCN)_6] \cdot 4H_2O$ (Zhdanov et. al. ⁴¹)
	Small Cell	Large Cell	
a	$14.45 \pm 0.02 \text{ \AA}$	29.02 \AA	14.18 \AA
c	$9.63 \pm 0.01 \text{ \AA}$	19.26 \AA	9.69 \AA
z	3	24	3
d_{calc}	1.67 g/cc		1.74 g/cc
d_{obs}	1.71 g/cc ⁴¹		1.71 g/cc
Possible Space Groups	$P\bar{3}m1$, $P\bar{3}1m$, $P31m$, $P3m1$, $P321$, $P312$ or $P\bar{3}$.	-	$P\bar{3}m1$
	$K_3[Mo(NCS)_6] \cdot 4H_2O$ (This work)		$K_3[Mo(NCS)_6] \cdot H_2O \cdot CH_3COOH$ (Knox and Eriks ⁶⁰)
	Small Cell	Large Cell	
a	$14.51 \pm 0.02 \text{ \AA}$	29.02 \AA	$13.547 \pm 0.002 \text{ \AA}$
b	-	-	$8.568 \pm 0.002 \text{ \AA}$
c	$9.82 \pm 0.01 \text{ \AA}$	19.64 \AA	$9.660 \pm 0.001 \text{ \AA}$
z	3	24	2
d_{calc}	1.76 g/cc		1.69 g/cc
d_{obs}	-		1.85 g/cc
Space Group	As for $K_3Cr(NCS)_6 \cdot 4H_2O$		
Mo-N bond			$2.088 \pm 0.019 \text{ \AA}$

and gave a residual factor of $R = 96\%$, a value patently wrong if the model had been even partially correct. This structure factor calculation was carried out in the triclinic space group $P\bar{1}$ on data taken only from the hk0 section of the reciprocal lattice.

A three dimensional Patterson function was calculated by likewise simulating the trigonal symmetry in $P\bar{1}$ (triclinic). Sections from $z = 0$ to $z = 1/2$ with intervals of $1/40$ were calculated along $[001]$. Sections containing likely peaks were contoured by hand. The interpretation proved difficult. The presence of Cr, S and K atoms, all of approximately the same atomic number gave rise to many vector peaks of similar heights, although the presence of peaks on the Harker line $[001]$ suggests that most of this scattering matter is located in planes with y approximately 0, $1/4$ and $1/2$. The fact, however, that there are only 3 Cr atoms present in this unit cell made interpretation somewhat easier. Considering space group $P\bar{3}$ which covers in the general case both the D_{3d} space groups $P\bar{3}lm$ and $P\bar{3}ml$; the Cr atoms can be located in 3-fold, 3(f) or 3(e) positions or in a combination of 1(a) (or 1(b)) and either 2(c) or 2(d) positions. The presence of appropriate interatomic vectors in the Patterson allows for either 3(f), 3(e) or a combination of 1(a) and 2(d) (the 1(b) and 2(d) combination is equivalent). The 3(f) and 3(e) positions were later ruled out, as any possible K or S positions provided by the space group did not generate the necessary Cr-K or Cr-S vectors in the Patterson. Thus the three chromium atoms can be arbitrarily placed at 1(a) (0,0,0) and 2(d) ($1/3$, $2/3$, z) where $z \approx 1/2$. With the Cr atoms fixed, the next step was to search for possible Cr-S vectors at either a theoretical Cr-SCN bond distance of about 2.8 \AA or a Cr-NCS bond distance of about 5.2 \AA from the origin in the Patterson. There were no suitable peaks within 3 \AA of the origin and this was taken to rule out the possibility of Cr-SCN bonding in the complex ion. At a distance of approximately 5.2 \AA from the Patterson origin a number of possible peaks were located. A possible allocation of

three 6(g) positions was made for the 18 S atoms present. This gave a D_{3d} type arrangement of the CrS_6 octahedra with respect to the c -axis. This arrangement also gave trigonal prismatic arrangements of S atoms (Fig. 2.3) about locations which could be occupied by K^+ ions similar to those in the structure of $K_3[Mo(NCS)_6] \cdot H_2O \cdot CH_3COOH$ ⁶⁰. Twelve such locations for the 9 possible K^+ ions were thus made available in two 6(g) positions. This suggested a form of disorder where one of these positions could be occupied half the time by K^+ ions and half the time by water molecules, giving a correct stoichiometry with respect to the 9 K^+ ions. This possible arrangement is shown in Fig. 2.4 by projection down [001]. The large hexagonal prism shaped holes created between two sets of six sulphur atoms could provide locations for the other 9 H_2O molecules, (Fig. 2.5), a fact that could account for the ease of removal of 3 waters of crystallization by dehydration from each molecule and the difficulty of removing the last water. Three such hexagonal prismatic holes occur and it could be expected that each will contain 3 waters to maintain the centrosymmetry of the model. To locate three water molecules in the prism centered on [001] the positions 1(b) (0,0, 1/2) and 2(c) (0,0,z) with $z \approx 1/4$ would have to be used. This would give a H_2O-H_2O distance of $< 2.4 \text{ \AA}$ which is less than the 2.56 \AA ²³ known for strong H_2O-H_2O H-bonding, and give $Cr-OH_2$ as 2.4 \AA which is greater than the $Cr-OH_2$ bond length of 2.1 \AA reported in octahedral complexes. Placing water molecules in the other two prisms causes identical problems. The noncentrosymmetric space groups likewise offer no solution to this dilemma. Structure factors calculations were carried out based on models for the $K_3CrS_6 \cdot H_2O$ portion of the structure and allowing for different types of disorder positions for potassium ions and the water molecule. The best residual factor obtained from these was a model with $R = 49\%$. Subsequent Fourier and difference Fourier calculations revealed possible locations for the N and C atoms and gave a model with $R = 42\%$. Difficulties encountered in calculating the Fourier in $P\bar{1}$ made it hard to

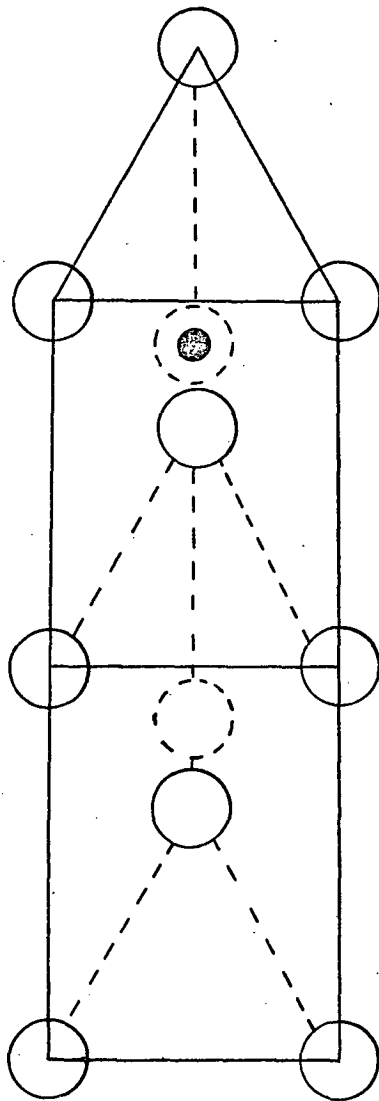


Fig. 2.3 Trigonal prism of sulphur atoms
 $K_3[Cr(NCS)_6] \cdot 4H_2O$



S



K in $z \sim 0$



K and O in $z \sim \frac{1}{2}$

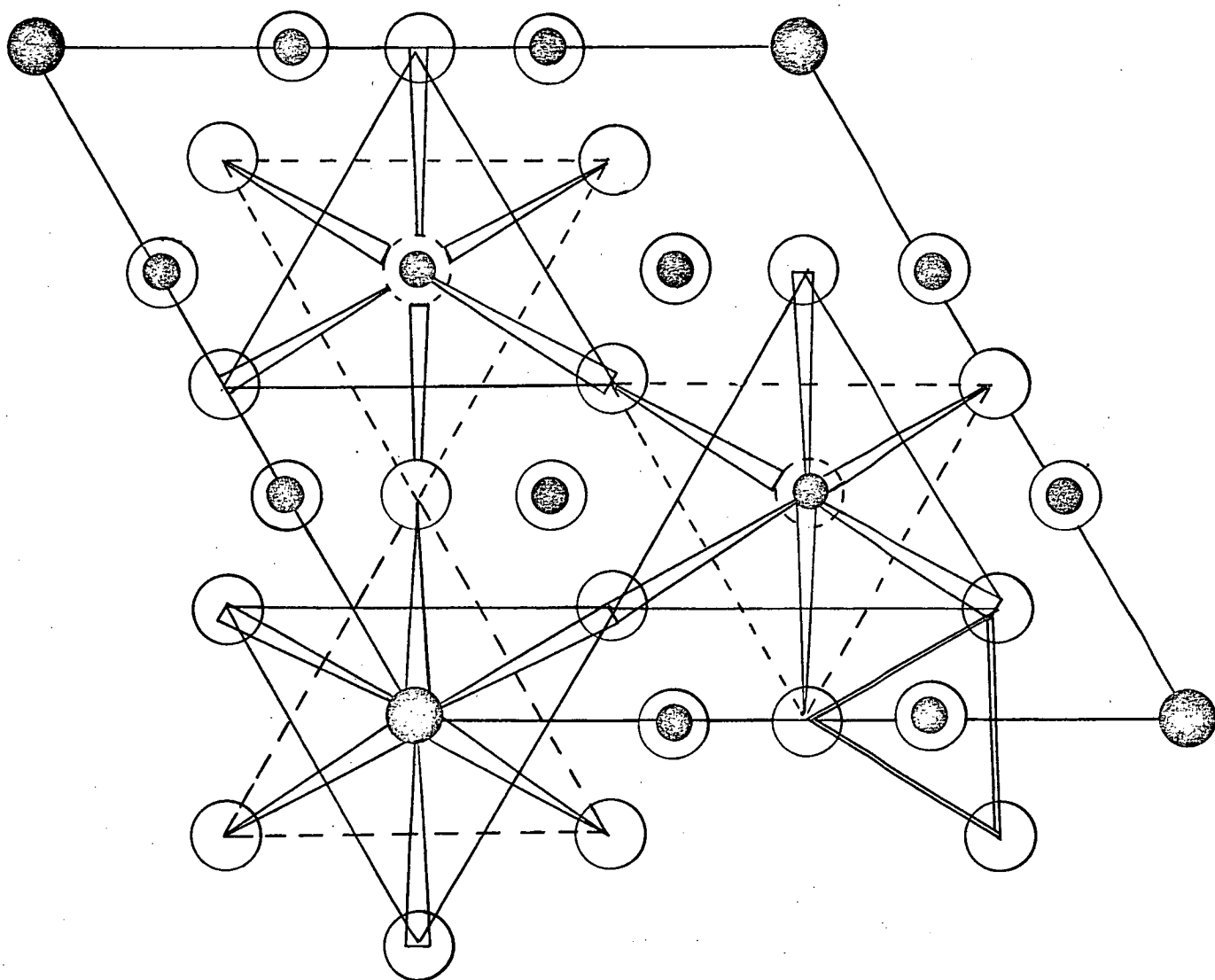
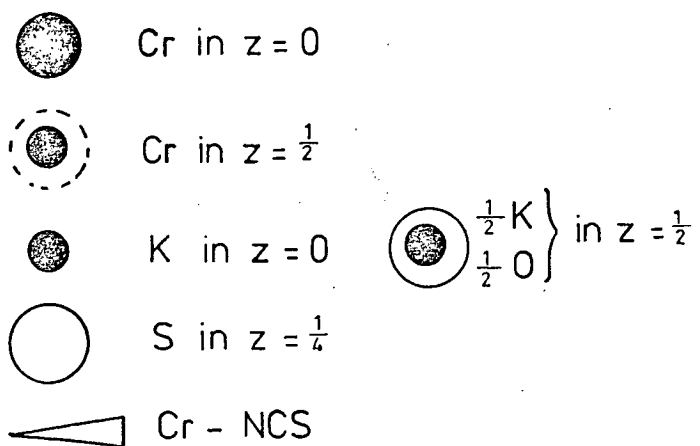


Fig. 2.4 Projection on [001] $K_3[Cr(NCS)_6] \cdot 4H_2O$: Possible Structure



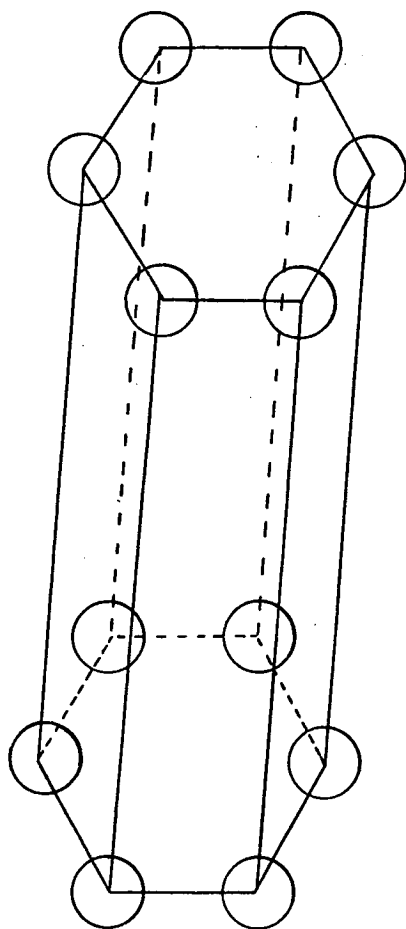


Fig. 2.5 Hexagonal prism of sulphur atoms
 $K_3[Cr(NCS)_6] \cdot 4H_2O$



fix possible positions for the water molecules. The Fourier map based on the $K_3[Cr(NCS)_6] \cdot H_2O$ model showed peaks for all atoms inserted, with reasonable correlation between peak heights and atomic number, but also with many ghost peaks of atoms particularly in levels with $z = 0$ and $z = \frac{1}{2}$. The difference Fourier gave reasonably flat contours at atom locations with the rest of the map being devoid of any peaks in possible water molecule locations.

Cycles of block diagonal least squares refinement tried on the structure factors derived from this model reduced R to 32%. Attempts to include isotropic temperature factors in the refinement were unsuccessful as large shifts were attributed to these temperature factors for most of the atoms. The atomic parameters at which refinement was terminated are shown in Table 2.3. A comparison of observed and calculated structure factors is given in Appendix 3 as Table A.3.1. The observed intensity data for $K_3[Cr(NCS)_6] \cdot 4H_2O$ corresponding to the weak layer lines about the c -axis is also given in Appendix 3 as Table A.3.3.

Chronologically data were collected first for the chromium compound. When structure determination attempts ran into difficulties attention was switched to the molybdenum compound, $K_3[Mo(CNS)_6] \cdot 4H_2O$. It was hoped that the relatively heavy metal (Mo) would facilitate solution of the crystal structure.

2.4. Structure Analysis : $K_3[Mo(CNS)_6] \cdot 4H_2O$

The compound was prepared by Skabo following the method of Maas and Sand⁴³. The crystals were similar in shape with those of the analogous chromium compound but were orange in colour. Crystal selection and mounting were carried out as for $K_3[Cr(NCS)_6] \cdot 4H_2O$. Oscillation photographs taken about both the a and c -axes also showed weak intermediate layer lines. Unit cell dimensions were determined as for $K_3[Cr(NCS)_6] \cdot 4H_2O$. Relevant

TABLE 2.3

Atomic Coordinates : $K_3[Cr(NCS)_6] \cdot 4H_2O$ at R = 32% (As for space group $P\bar{3}$)

Atom	x	y	z
Cr 1	0	0	0
Cr 2	0.333	0.667	0.431
S 1	0.167	0.333	0.214
S 2	0.500	0	0.299
S 3	0.333	0.167	0.232
N 1	0.931	0.069	0.097
N 2	0.265	0.735	0.338
N 3	0.598	0.402	0.433
C 1	0.890	0.110	0.175
C 2	0.224	0.776	0.285
C 3	0.557	0.443	0.382
K 1	0.372	0	0
K 2 (half occupancy)	0.296	0	0.5
H ₂ O 1 (half occupancy)	0.296	0	0.5
H ₂ O 2	0	0	0.400
H ₂ O 3	0.333	0.667	0.205
H ₂ O 4	0.333	0.667	0.528

powder data are given in Table 2.4 while unit cell dimensions are recorded in Table 2.2. Comparison of powder and single crystal X-ray photographs clearly shows the compound to be isomorphous with $K_3[Cr(NCS)_6] \cdot 4H_2O$, and hence the molybdenum compound should be written as $K_3[Mo(NCS)_6] \cdot 4H_2O$.

Integrated intensity data from strong layer lines were recorded for hkn ($n = 0-5$) and $nk\ell$ ($n = 0-5$), and processed in identical fashion with the data from $K_3[Cr(NCS)_6] \cdot 4H_2O$. Weak layer line data were recorded but not measured.

The structure determination followed similar lines to that discussed for the chromium compound. The R-factor at which structure refinement was terminated stood at 38%. The atomic parameters as they were at this stage are given in Table 2.5. Observed and calculated structure factors are listed in Appendix 3 as Table A.3.3.

2.5 Conclusion

The discussion given in Section 2.3 of attempts at structure solution has been made with the benefit of hindsight. Since termination of the structure determinations, the author has carried out several other X-ray crystal structure analyses which are reported in later chapters of this thesis.

What has emerged from this research on thiocyanates?

1. The refined unit cell of potassium hexathiocyanatochromate(III) tetrahydrate, $K_3[Cr(NCS)_6] \cdot 4H_2O$ (with $z = 3$) is slightly different from that reported by Zhdanov, Zvonkova and Glushkova⁴¹.
2. Unit cell dimensions are reported for the first time for potassium hexathiocyanatomolybdate(III) tetrahydrate, $K_3[Mo(NCS)_6] \cdot 4H_2O$.
3. A comparison of powder and single crystal X-ray photographs shows that the two compounds are isomorphous.

TABLE 2.4

X-Ray Powder Data : $K_3[Mo(CNS)_6] \cdot 4H_2O$ Cu K_α radiation : $\sin^2 \theta \times 10^4$

(Estimated intensities : s = strong, m = medium, w = weak, b = broad)

$\sin^2 \theta_{obs}$	Estimated Intensity	Small Cell		Large Cell	
		$\sin^2 \theta_{calc}$	Index	$\sin^2 \theta_{calc}$	Index
99.1	s	99.1	1 0 1	99.1	2 0 2
				99.6	3 0 0
112.9	w	112.8	1 1 0	112.2	2 2 0
173.9	w	174.4	1 1 1	173.9	2 2 2
176.5	vw	-	-	176.3	2 0 3
					3 2 0
211.7	m	211.9	2 0 1	211.3	4 0 2
215.9	vwb	-	-	211.8	4 1 1
325.2	s	324.9	2 1 1	323.5	4 2 2
337.8	vw	338.4	3 0 0	335.3	4 1 3
				336.6	6 0 0
357.3	w	358.8	1 1 2	359.1	2 2 4
361.7	vw	-	-	364.7	5 2 0
				365.4	4 3 1
399.0	vw	399.9	3 0 1	398.3	6 0 2
403.2	w	-	-	402.1	6 1 0
451.0	m	451.2	2 2 0	448.8	4 4 0
457.6	s	-	-	451.2	5 3 0
					2 1 5
506.6	w	509.2	2 1 2	507.4	3 1 5
				508.7	4 2 4
514.6	w	512.7	2 2 1	510.4	4 4 2
				512.9	7 0 2

TABLE 2.4 (Cont.)

582.7	s	584.4	3 0 2	582.2	4 1 5
				583.5	6 0 4
				584.0	1 1 6
588.3	m	591.1	1 0 3	589.1	6 3 0
				590.1	5 3 3
698.8	m	697.2	2 2 2	698.0	8 1 1
				698.1	7 0 4
				698.1	5 3 4
708.4	w	714.4	1 0 3	705.1	4 0 6
				709.3	5 4 3
				710.6	6 4 0
779.7	vw	775.9	3 2 1	772.3	6 4 2
				779.9	7 1 4
789.8	vw	-	-	787.9	6 1 5
				789.3	5 0 6
890.1	w		3 0 3	892.1	6 0 6

TABLE 2.5

Atomic Coordinates $K_3[Mo(NCS)_6] \cdot 4H_2O$ at R = 38% (As for space group $P\bar{3}$)

Atom	x	y	z
Mo 1	0	0	0
Mo 2	0.167	0.333	0.457
S 1	0.167	0.333	0.188
S 2	0.500	0	0.265
S 3	0.333	0.167	0.287
N 1	0.883	0.068	0.169
N 2	0.272	0.735	0.299
N 3	0.583	0.402	0.505
C 1	0.873	0.109	0.147
C 2	0.233	0.776	0.321
C 3	0.570	0.443	0.322
K 1	0.378	0	0
K 2 (half occupancy)	0.303	0	0.5
H ₂ O 1 (half occupancy)	0.303	0	0.5
H ₂ O 2	0	0	0.400
H ₂ O 3	0.333	0.667	0.247
H ₂ O 4	0.333	0.667	0.599

4. The presence of weak intermediate layer lines on oscillation photographs of both compounds suggests that disorder or superlattice phenomena occur in their crystal lattices.

5. Structure determination and refinement on both compounds is incomplete at this point. There is, however, sufficient evidence to favour metal to nitrogen bonding in the $[M(NCS)_6]^{3-}$ (M=Mo or Cr) complex ions of both compounds. This is contrary to metal to sulphur bonding postulated by Zhdanov et al⁴¹ for $K_3[Cr(SCN)_6] \cdot 4H_2O$, but agrees with the bonding found in $K_3[Mo(NCS)_6] \cdot H_2O \cdot CH_3COOH$ ⁶⁰ and in the reineckates⁵⁰⁻⁵³.

6. There is also evidence to show that there is six-fold coordination of thiocyanate ligands around the central metal, M(III) ions. There is no evidence for coordinate central metal to water bonding.

With the completion in the near future of a full suite of crystallographic computer programs in this Department it should be possible to refine structure factors and calculate Fouriers directly in trigonal symmetry. It would then be possible to make further attempts at solving these structures.

The information to be gained from a complete structure determination on $K_3[Cr(NCS)_6] \cdot 4H_2O$ and $K_3[Mo(NCS)_6] \cdot 4H_2O$ in the light of the problems involved would not, however, be sufficient justification for the effort required. It would, of course, be interesting to find out the cause of the weak layer lines, but other points of interest as discussed in Section 2-1 could well be obtained from a study of other similar compounds. This has, in effect, been done in part by Knox and Eriks⁶⁰ with $K_3[Mo(NCS)_6] \cdot H_2O \cdot CH_3COOH$.

Chapter 3

Crystal and Molecular Structures of Six $A_2[M^{I,III}Cl_5H_2O]$ Compounds

(A = K, NH_4 , Rb, or Cs; M = Fe or Mo)

3.1. Introduction

Compounds of the type $A_2[MX_5H_2O]$ (X = halide) have been known for some time⁶¹. However, it was not until 1945 that crystal structure determinations carried out on $K_2[FeCl_5H_2O]$ ⁶² and $(NH_4)_2[FeCl_5H_2O]$ ⁶³ showed that both crystallized with orthorhombic symmetry in space group Pnma, a structure type of which $[Rh(NH_3)_5Cl]Cl_2$ ⁶⁴ was already a known member. Later $K_2[RuCl_5H_2O]$ ⁶⁵, $(NH_4)_2[InCl_5H_2O]$ ⁶⁶ and $Cs_2[TlCl_5H_2O]$ ⁶⁷ were shown to have the same structure. However, in 1966 Hopkins et al⁶⁸ showed that $Cs_2[RuCl_5H_2O]$ adopted a different orthorhombic structure, crystallizing with space group Amam.

Structural studies in these laboratories on compounds of the $A_2[MX_5H_2O]$ type have been in progress for some years, and a wide range of such compounds have been prepared, and analysed mainly by far infrared and nuclear quadrupole resonance (n.q.r.) spectroscopy^{61, 69-71}. Far infrared spectra of these type of compounds showed definite trends in M-O and M-Cl stretching frequencies, in compounds with the same central metal and different cations, and in groups of compounds with the same cations and different central metal ions. N.q.r. studies showed several anomalies.

Crystal structure studies were commenced on six compounds:

$K_2MoCl_5H_2O$, $(NH_4)_2MoCl_5H_2O$, $Rb_2MoCl_5H_2O$, $Cs_2MoCl_5H_2O$, $Rb_2FeCl_5H_2O$ and $Cs_2FeCl_5H_2O$. These structures would then provide data for two comparative series of $A_2[MCl_5H_2O]$ compounds. From this data it was hoped to be able to explain the far infrared and n.q.r. results. The other major object in carrying out these crystal structure determinations was to see if the newly prepared molybdenum compounds can be classified into the two structural types

already known. The results of this classification and the structures of the iron salts could then be used to predict the structures of other analogous compounds.

3.2. Experimental

3.2.1. Preparation and Crystal Selection

The iron compounds were prepared by passing HCl gas through a concentrated HCl solution containing stoichiometric amounts of the alkali metal chloride and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The molybdenum compounds were precipitated by similar procedures. The compounds were prepared by Podmore and Stoessiger in these laboratories^{61,71}. All six compounds were recrystallized from warm concentrated HCl solution as clear orange needles. Rapid recrystallization was found to be the best process for growing suitable small crystals. The crystals selected for X-ray studies were all of approximate dimensions 0.2 mm x 0.1 mm x 0.1 mm.

It is proposed to describe the method used for data collection and structure determination of a representative compound, $\text{K}_2\text{MoCl}_5\text{H}_2\text{O}$. Variations encountered in the five other cases will then be discussed.

A crystal of $\text{K}_2\text{MoCl}_5\text{H}_2\text{O}$ was selected and mounted along the orthorhombic b -axis by gluing it with shellac to a glass fibre. This fibre was then set up on a goniometer head and mounted on a Weissenberg camera.

3.2.2. Data Collection

The cell parameters were obtained initially from oscillation and zero-level Weissenberg photographs, and refined on X-ray powder data (Table 3.1) collected on a Philips powder diffractometer using Cu K_α radiation and KCl as an internal calibrant. The powder work was carried out in collaboration with Podmore⁶¹. Crystallographic data for the six compounds studied in this work and for analogous compounds reported in the literature are given in Table 3.2.

TABLE 3.1

X-ray Powder Data

 $(\sin^2 \theta \times 10^4)$

$K_2[MoCl_5 \cdot H_2O]$			$(NH_4)_2[MoCl_5 \cdot H_2O]$		
$\sin^2 \theta_{obs.}$	$\sin^2 \theta_{calc.}$	Index	$\sin^2 \theta_{obs.}$	$\sin^2 \theta_{calc.}$	Index
177.7	178.4	0 1 1	146.2	146.8	1 0 1
187.0	188.2	2 1 0	175.1	175.9	0 1 1
209.9	209.9	1 1 1	182.3	183.1	2 1 0
240.5	241.7	2 0 1	206.4	206.7	1 1 1
397.2	397.3	1 2 1	238.0	239.3	2 0 1
461.8	461.3	3 1 1	394.8	393.4	3 0 1
494.2	495.2	1 0 2	452.7	453.2	3 1 1
500.7	503.0	4 0 0	478.1	478.6	2 2 1
616.8	618.9	4 0 1	495.0	494.9	1 0 2
649.9	648.8	3 2 1	635.0	632.7	3 2 1
679.5	678.3	0 3 1	663.7	661.7	2 3 0
716.0	713.7	0 2 2	705.6	703.4	0 2 2
745.5	745.1	1 2 2	739.6	741.4	3 0 2
803.8	804.1	2 3 1	889.8	886.4	5 0 1
838.8	839.4	2 2 2	958.5	957.2	0 4 0
873.5	868.9	4 2 1	1079.3	1080.5	2 4 0
900.2	901.8	5 0 1	1233.4	1234.5	5 0 2
963.6	966.7	4 0 2	1299.5	1294.3	5 1 2
1002.1	999.8	0 4 0	1471.8	1473.8	5 2 2
1078.3	1074.8	1 0 3	1572.2	1573.5	6 0 2
1247.8	1247.6	6 0 1	1705.9	1705.9	2 3 3
1310.0	1310.0	6 1 1			
1387.6	1388.8	3 1 3			
1498.0	1497.6	6 2 1			
1658.3	1657.9	6 1 2			
1745.4	1746.5	3 4 2			

TABLE 3.1 (Cont.)

$\text{Rb}_2[\text{MoCl}_5\text{H}_2\text{O}]$			$\text{Rb}_2[\text{FeCl}_5\text{H}_2\text{O}]$		
$\sin^2\theta_{\text{obs.}}$	$\sin^2\theta_{\text{calc.}}$	Index	$\sin^2\theta_{\text{obs.}}$	$\sin^2\theta_{\text{calc.}}$	Index
174.9	175.1	0 1 1	178.1	179.1	0 1 1
181.6	180.2	2 1 0	185.1	185.4	2 1 0
204.4	205.1	1 1 1	212.4	210.3	1 1 1
387.6	385.7	1 2 1	240.5	242.5	0 2 0
478.1	479.8	4 0 0	393.8	392.2	1 2 1
487.9	489.2	1 0 2	485.6	485.8	2 2 1
629.9	625.6	3 2 1	498.4	499.1	4 0 0
661.6	661.8	2 3 0	507.5	505.3	1 0 2
698.9	700.4	0 2 2	617.2	617.6	4 0 1
729.5	729.5	3 0 2	642.7	641.8	3 2 1
963.1	963.4	0 4 0	669.4	670.4	2 3 0
1621.4	1621.5	6 3 0	714.7	716.6	0 2 2
1696.0	1695.9	2 3 3	749.6	747.8	1 2 2
			861.7	860.1	4 2 1
			972.5	973.2	4 0 2
			1311.9	1314.6	5 1 2
			1366.5	1365.5	6 2 0
			1473.1	1475.3	1 4 2
			1588.1	1587.6	4 4 1
			1647.2	1647.1	7 0 1
			1725.0	1724.8	3 4 2

TABLE 3.1 (Cont.)

$\text{Cs}_2[\text{MoCl}_5\text{H}_2\text{O}]$			$\text{Cs}_2[\text{FeCl}_5\text{H}_2\text{O}]$		
$\sin^2\theta_{\text{obs.}}$	$\sin^2\theta_{\text{calc.}}$	Index	$\sin^2\theta_{\text{obs.}}$	$\sin^2\theta_{\text{calc.}}$	Index
166.3	168.1	0 2 1	168.8	170.1	0 2 1
280.5	281.4	1 3 0	285.1	285.8	1 3 0
360.8	360.4	0 0 2	316.9	317.1	0 4 0
370.0	371.5	1 3 1	363.4	363.2	0 0 2
423.1	423.1	2 0 0	376.6	376.6	1 3 1
641.8	641.7	1 3 2	428.4	429.6	2 0 0
673.0	672.5	0 4 2	490.1	490.4	1 1 2
687.0	683.6	1 5 1	650.4	649.0	1 3 2
703.9	702.4	0 6 0	681.2	680.4	0 4 2
734.5	735.2	2 4 0	714.2	713.6	0 6 0
787.7	783.4	2 0 2	745.9	746.8	2 4 0
954.4	953.9	1 5 2	792.4	792.9	2 0 2
1092.4	1092.2	1 3 3	1108.2	1110.0	2 4 2
1155.8	1151.9	1 7 1	1169.8	1169.4	1 7 1
1215.0	1215.6	2 6 1	1238.5	1235.9	3 3 1
1248.9	1248.7	0 8 0	1268.5	1268.5	0 8 0
1341.5	1338.8	0 8 1	1458.3	1462.2	3 5 0
1442.4	1441.4	0 0 4	1508.3	1508.3	3 3 2
1487.3	1487.9	3 3 2	1628.5	1631.8	0 8 2
1512.3	1513.2	0 6 3	1713.8	1712.9	1 9 0
1606.0	1609.9	0 8 2	1739.5	1738.7	1 3 4

TABLE 3.2

Crystallographic Data

 $A_2[MCl_5H_2O]$ compounds

Cell edges in angstroms. Volume in \AA^3 . Density g/cc. Standard deviations ()

	$K_2[MoCl_5H_2O]^*$	$(NH_4)_2[MoCl_5H_2O]^*$	$Rb_2[MoCl_5H_2O]^*$	$Cs_2[MoCl_5H_2O]^*$
a	13.738(6)	13.875(6)	14.066(6)	7.432(5)
b	9.744(5)	9.958(5)	9.926(5)	17.301(8)
c	7.154(5)	7.151(5)	7.186(5)	8.083(5)
V	957.7	988.0	1003.3	
Space Group	4 Pnma	4 Pnma	4 Pnma	4 Cmcm
D_{obs}	-	-	-	-
D_{calc}	2.56	2.20	3.07	3.30
	$K_2[FeCl_5H_2O]^{62}$	$(NH_4)_2[FeCl_5H_2O]^{63}$	$Rb_2[FeCl_5H_2O]^*$	$Cs_2[FeCl_5H_2O]^*$
a	13.75(2)	13.78	13.764(6)	7.490(5)
b	9.92(2)	9.85	9.917(5)	17.438(8)
c	6.93(2)	7.09	7.080(5)	8.115(5)
V	945.25	962.35	966.4	
Z	4	4	4	4
Space Group	Pnma	Pnma	Pnma	Cmcm
D_{obs}	-	1.99		
D_{calc}			2.91	3.49
	$K_2[RuCl_5H_2O]^{65}$	$(NH_4)_2InCl_5H_2O^{66}$	$Cs_2[TlCl_5H_2O]^{67}$	$Cs_2[RuCl_5H_2O]^{68}$
a	13.53(5)	14.10(5)	14.36	7.400(4)
b	9.55(5)	10.17(5)	10.61	17.289(8)
c	6.96(3)	7.16(5)	7.38	7.986(5)
V	899.31	1026.72	1124.41	1021.92
Z	4	4	4	4
Space Group	Pnma	Pnma	Pnma	Amam
D_{obs}	-	-	-	-
D_{calc}	2.76			3.65

* This work.

A trial, zero level, non-integrated Weissenberg photograph showed the diffraction spots to be of reasonably regular shape. Because of this, it was decided that the collection of integrated data was unnecessary. This reduced the collection time by approximately one half.

A total of 216 observed reflections for five levels hnl ($n = 0-4$) were recorded by the equi-inclination Weissenberg technique using Cu K_α radiation and 4-film packs. Extension of data collection could have been made for higher levels and about another axis. This was not carried out, however, because the $h5l$ level exhibited diffraction spots of poor resolution. Also the data collected about the one axis provides sufficient data for the structure determination.

The intensities of these observed reflections were measured visually against a standard scale and were corrected for Lorentz and polarisation factors. Because of the small crystals used, no absorption corrections were considered necessary.

Inspection of the Weissenberg photographs revealed the compound to be orthorhombic with the following reflections absent : $0k\bar{l} : k + l \text{ odd}$; $hk0 : h \text{ odd}$.

The space group corresponding to this absence pattern is Pnma .

3.3. Structure Analyses: $\text{K}_2\text{MoCl}_5\text{H}_2\text{O}$

The X-ray powder pattern for $\text{K}_2\text{MoCl}_5\text{H}_2\text{O}$ is very similar to that of $\text{K}_2[\text{FeCl}_5\text{H}_2\text{O}]$ reported by Podmore⁶¹. This suggests that the two compounds are isomorphous. In order to confirm this, and also to gain increased familiarity with the Patterson technique, it was decided to calculate a three-dimensional Patterson function. The calculation was made in the Patterson group Pmmm . The three Harker planes of the crystal space group Pnma are, $(\frac{1}{2}yz)$, $(x\frac{1}{2}z)$ and $(xy\frac{1}{2})$ and the Harker lines are $(x\frac{1}{2}\frac{1}{2})$, $(0y0)$ and $(\frac{1}{2}0z)$.

In this centrosymmetric case all the required Patterson sections were calculated with divisions of $1/40$ b from $y = 0$ to $y = \frac{1}{2}$. Two sections with $y = 0$ and $y = \frac{1}{4}$ are shown as Figs. 3.1 and 3.2.

The Mo^{3+} ions must occupy a four-fold position and since two of the three available positions, 4(a) and 4(b) require vectors $(0, 1/2, 0)$, $(1/2, 0, 1/2)$ and $(1/2, 1/2, 1/2)$ these positions can be eliminated because of the complete absence of the $(1/2, 0, 1/2)$ vector. For the position 4(c), one would expect Mo-Mo vectors to occur in the Harker plane $(x\frac{1}{2}z)$ and on the lines $(x\frac{1}{2}\frac{1}{2})$ and $(\frac{1}{2}Oz)$. The largest and most probable peak in the Harker plane is that at $(0.22, 0.5, 0.6)$ and the related Harker line peaks occurs at $(0.72, 0.5, 0.5)$ and $(0.5, 0, 0.1)$. This makes it possible to set up three expressions:

$$\begin{aligned} \pm 2x, 1/2, \pm 2z &= 0.22, 0.5, 0.6 \\ 1/2 \pm 2x, 1/2, 1/2 &= 0.72, 0.5, 0.5 \\ 1/2, 0, 1/2 \pm 2z &= 0.5, 0, 0.1 \end{aligned}$$

These were solved to give a possible Mo position at $(0.11, 0.25, 0.3)$.

The only ions which can occupy eight-fold general positions 8(d), are K^+ and some of the chlorines. The smallest of these, the K^+ ion can be expected to have a radius close to its ionic radius of about 1.33 \AA and since the y coordinate must be smaller than 0.12 owing to the mirror planes $(x\frac{1}{4}z)$ and $(x\frac{3}{4}z)$, then the K^+ and some of the chlorines must be sited near the planes (xOz) and $(x\frac{1}{2}z)$ and the other chlorines and the water molecule were thus expected to be situated exactly in the $(x\frac{1}{4}z)$ and $(x\frac{3}{4}z)$ planes.

Using the possible Mo position as a reference point a search was made in the Patterson planes (xOz) and $(x\frac{1}{4}z)$ for suitable Mo - K and Mo - Cl vectors. It was possible to assign the vectors shown in the appropriate maps (Figs. 3.1 and 3.2) in this fashion, and thus to arrive at a model for the structure to accommodate all the K, Mo and Cl atoms. It would have also been possible to arrive at a similar model by allocating coordinates to the atoms by analogy with the structure of $\text{K}_2[\text{FeCl}_5\text{H}_2\text{O}]$.⁶²

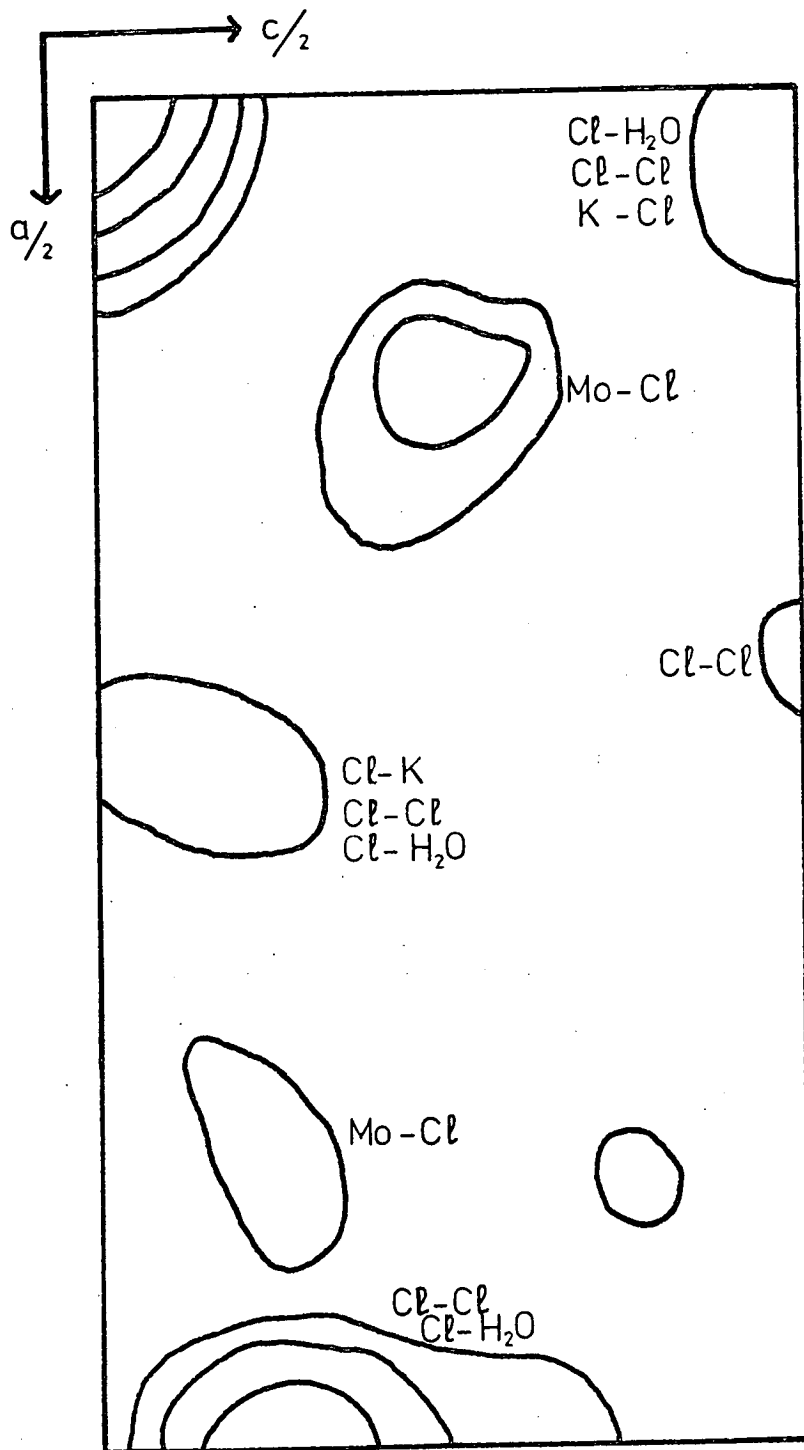


Fig. 3.1 Patterson Section $y=0$ $K_2MoCl_5 \cdot H_2O$ showing assigned interatomic vectors

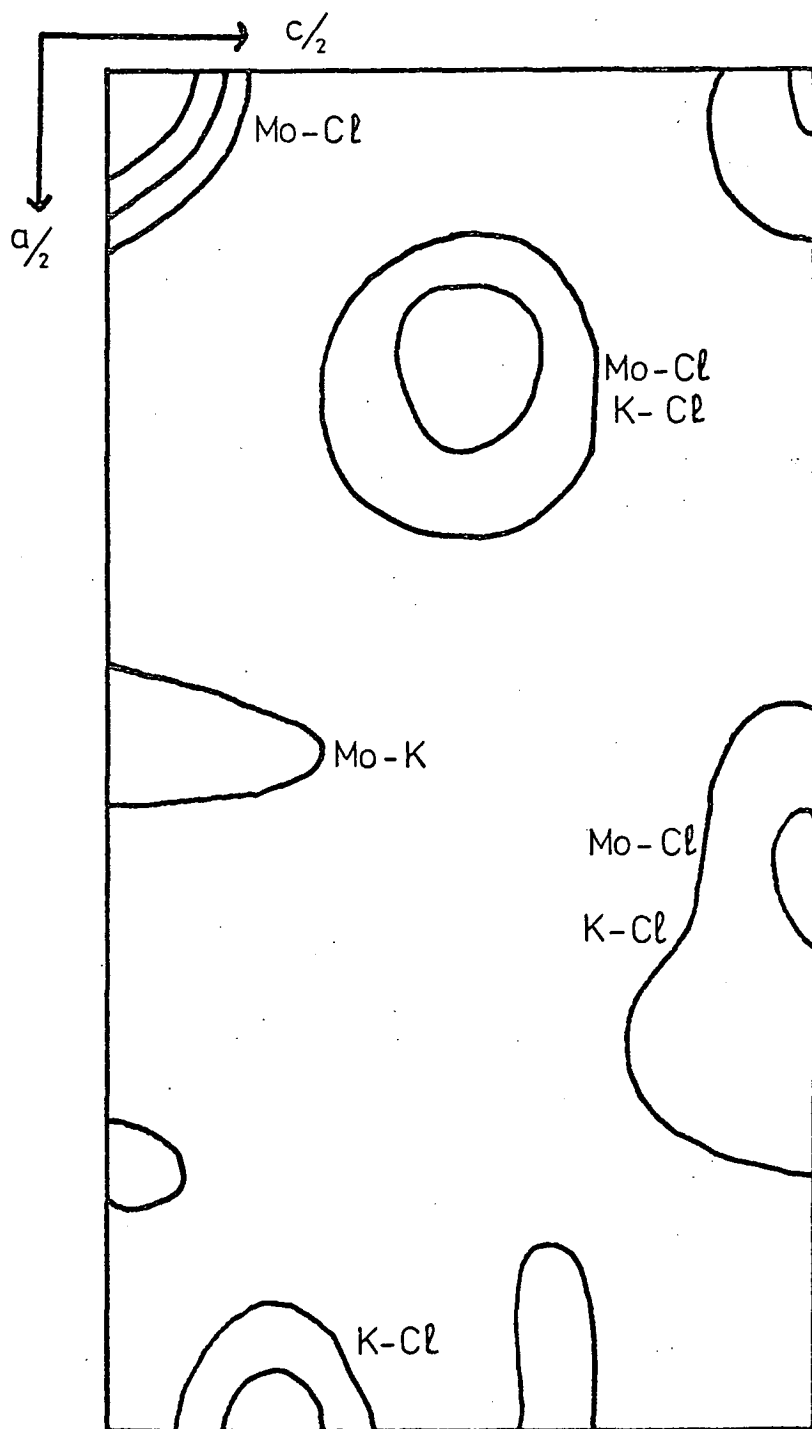


Fig. 3.2 Patterson Section $y = \frac{1}{4}$ $K_2MoCl_5H_2O$ showing assigned interatomic vectors

Structure Refinement

Structure factors, corresponding to the measured reflections, were calculated using the model derived from the Patterson function. The initial residual factor (R) after interlayer scaling was 24%. The signs of the calculated structure factors were used in conjunction with the observed structure factors to calculate three-dimensional Fourier and difference Fourier syntheses. As expected at this initial stage the relative heights of the Fourier peaks showed only very approximate correlation to atomic number. From an analysis of both maps it was possible to relocate various atoms by moving them up the peak gradient shown on the difference Fourier, and also to allocate positions to the remaining oxygen atoms. A further Fourier and difference Fourier were then calculated and since both of these were satisfactory, further refinement was carried out by the least squares method of correlating observed and calculated structure factors. This consisted of refining the function $R = \frac{\sum [|F_o| - |F_c|]}{\sum |F_o|}$ by use of the full matrix least squares method. Initially the interlayer scale factors and coordinates were put through one refinement cycle, the R factor reducing to 19%. Suitable trial isotropic temperature factors assigned to each atom were then included in the refinement. These temperature factors were obtained from the literature by using values for the same atoms found in similar environments in other crystal structures. A slight problem arose at this stage when the temperature factor for the oxygen atom went negative. It was decided to fix this temperature factor and continue. All other parameters refined successfully to an R factor of 14%. The oxygen temperature factor was then allowed to vary together with all other variables and a final refinement cycle reduced the R factor to 13%.

The correlation between F_{obs} and F_{calc} was then examined and observed data which showed marked variation from the calculated data were re-measured. It was found that some of the reflections had to be slightly

altered and that two of them had been mixindexed. These corrections were made to the data set and further least squares refinement gave a final R-factor of 9.8%. At this stage all shifts in parameters were within the values of the standard deviations.

In view of the overall accuracy of these structure determinations (see Section 1.5) this was taken as a satisfactory conclusion of the refinement process. It was decided, however, to run a test to see if it was possible to introduce and refine anisotropic temperature factors. These factors were initially derived from the isotropic temperature factors. The only refinement found possible was that of the cross diagonal parameters giving a final R-factor of 8.7%. The limits of error discussed elsewhere suggested that this small change in R-factor did not justify the introduction of anisotropic temperature factors. (Section 1.5).

Using the refined variables with $R = 9.8\%$ a final list of observed versus calculated structure factors was produced and these are listed in Appendix 3 Table A3.4. Final Fourier and difference Fouriers were calculated. At this stage the relative peak heights of atoms in the Fourier showed good internal correlation and the difference Fourier map was very flat, with no peaks exceeding half the minimum peak height of the smallest oxygen atom in the Fourier.

Final coordinates and isotropic temperature factors are shown in Table 3.3. Relevant bond lengths and angles are, for convenience, shown in the later discussion (Section 3.6) in Table 3.6.

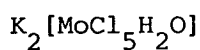
Description of the Structure of $K_2[MoCl_5H_2O]$

The structure of $K_2[MoCl_5H_2O]$ viewed in projection along $[010]$ is shown in Fig. 3.3. The four complex ions per unit cell are located in the four-fold set of equivalent Mo positions $(x, 1/4, z)$, $(\bar{x}, 3/4, \bar{z})$, $(1/2-x, 3/4, 1/2+z)$ and $(1/2+x, 1/4, 1/2-z)$ where $x = 0.112$ and $z = 0.314$. The octahedra consist of the

TABLE 3.3

Atomic Coordinates and Isotropic Temperature Factors

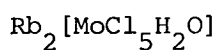
(Standard deviations in parenthesis)



Atom	Position	x	y	z	B
Mo	4(c)	0.1123(1)	0.25	0.3141(2)	0.97(3)
K	8(d)	0.3495(2)	-0.0002(4)	0.3639(3)	3.02(7)
Cl(1)	4(c)	0.0042(3)	0.25	0.0351(5)	2.77(10)
Cl(2)	4(c)	0.2516(3)	0.25	0.1162(5)	2.53(10)
Cl(3)	4(c)	0.2125(3)	0.25	0.5882(5)	2.72(10)
Cl(4)	8(d)	0.1044(2)	0.0056(12)	0.3124(5)	4.24(11)
O(H ₂ O)	4(c)	-0.0238(7)	0.25	0.4938(13)	2.56(22)

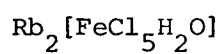


Atom	Position	x	y	z	B
Mo	4(c)	0.1117(1)	0.25	0.3131(2)	0.13(2)
N(NH ₄ ⁺)	8(d)	0.3524(4)	-0.0012(5)	0.3409(11)	2.13(14)
Cl(1)	4(c)	0.0038(2)	0.25	0.0420(5)	1.82(6)
Cl(2)	4(c)	0.2500(2)	0.25	0.1058(5)	1.29(6)
Cl(3)	4(c)	0.2191(2)	0.25	0.5786(6)	2.03(7)
Cl(4)	8(d)	0.1042(1)	0.0053(2)	0.3208(4)	1.62(4)
O(H ₂ O)	4(c)	0.9843(5)	0.25	0.4883(13)	2.34(17)



Atom	Position	x	y	z	B
Mo	4(c)	0.1124(1)	0.25	0.3118(2)	0.81(3)
Rb	8(d)	0.3552(1)	0.0002(2)	0.3475(2)	2.57(4)
Cl(1)	4(c)	0.0006(3)	0.25	0.0430(6)	2.43(12)
Cl(2)	4(c)	0.2485(3)	0.25	0.1076(6)	2.11(11)
Cl(3)	4(c)	0.2210(3)	0.25	0.5755(6)	2.66(11)
Cl(4)	8(d)	0.1036(2)	0.0073(10)	0.3171(4)	2.81(9)
O(H ₂ O)	4(c)	0.9880(7)	0.25	0.4931(14)	1.46(24)

TABLE 3.3 (Cont.)



Atom	Position	x	y	z	B
Fe	4(c)	0.1159(1)	0.25	0.3100(3)	1.05(4)
Rb	8(d)	0.3564(1)	-0.0005(1)	0.3431(1)	2.11(2)
Cl(1)	4(c)	0.0057(3)	0.25	0.0466(6)	1.74(7)
Cl(2)	4(c)	0.2452(2)	0.25	0.1044(5)	1.12(7)
Cl(3)	4(c)	0.2205(3)	0.25	0.5734(6)	1.71(8)
Cl(4)	8(d)	0.1046(2)	0.0085(2)	0.3212(4)	1.46(4)
O(H ₂ O)	4(c)	-0.0039(8)	0.25	0.4955(17)	1.16(14)

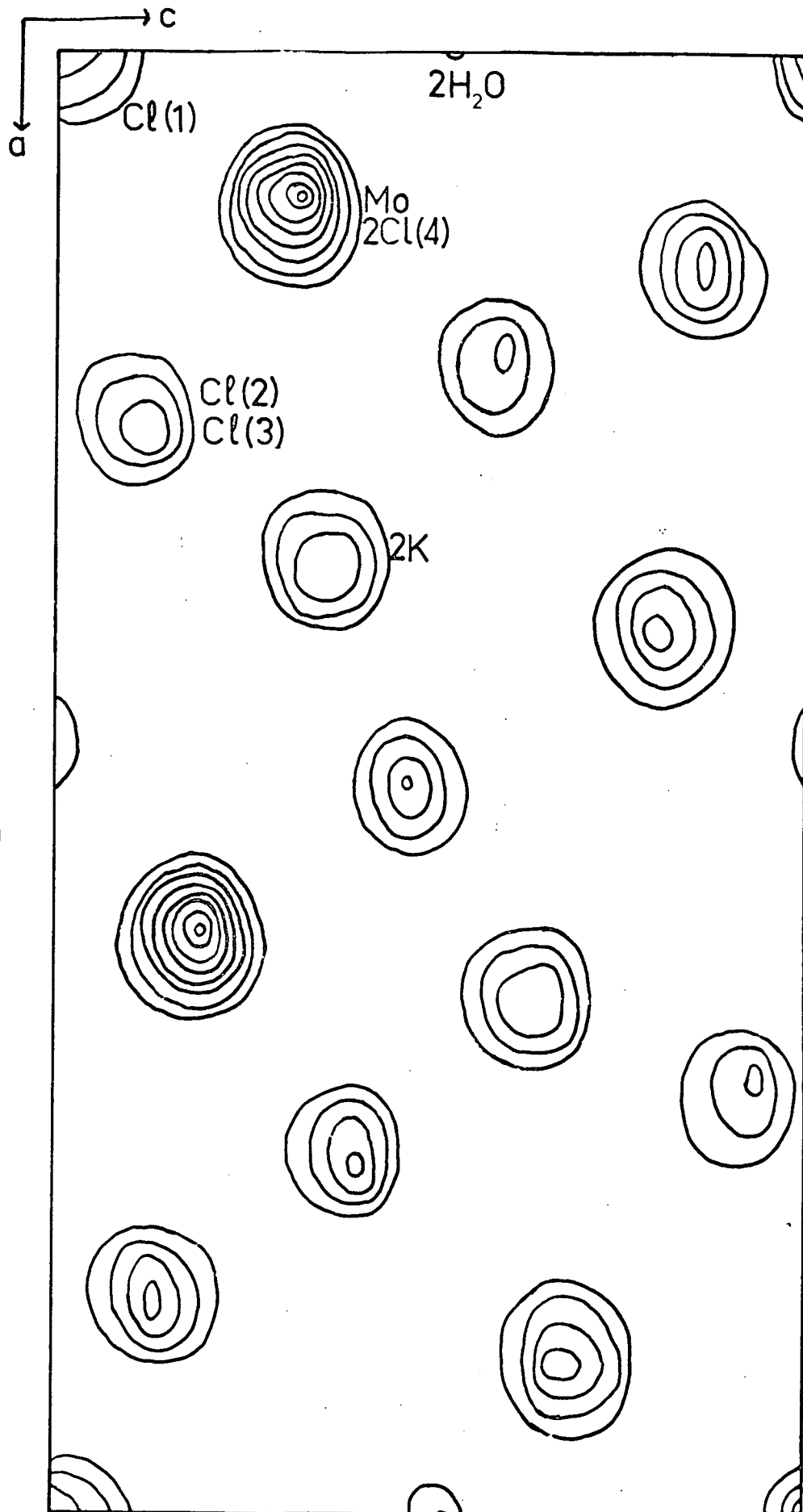


Fig. 3.3 FOURIER PROJECTION [010]
 $K_2[MoCl_5H_2O]$

central metal ion surrounded by three chlorines and the water molecule in the plane, with the two remaining chlorines situated above and below the central metal. The slightly distorted $[\text{MoCl}_5\text{H}_2\text{O}]^{2-}$ units are oriented with the Cl-Mo-H₂O axis in the plane with $y = \frac{1}{4}$ at an angle of approximately 90° to the $\frac{b}{a}$ axis.

The K^+ ions are situated in an eight-fold general position (x,y,z) with $y = 0$ and are surrounded by a distorted cube of six chlorine atoms and two water molecules.

The overall structure is thus a packing of K^+ ions and $[\text{MoCl}_5\text{H}_2\text{O}]^{2-}$ ions. That this electrostatic attraction provides the major bonding force linking the octahedra through K^+ ions is further demonstrated by the fact that possible H-bonded links between water molecules of one octahedral group and either water or chlorines of another complex ion can be regarded as minimal, because the shortest H₂O-Cl distance outside the complex ion is 3.892 Å and the shortest H₂O-OH₂ distance is 4.051 Å. Significant hydrogen bonding could have been expected to occur if the H₂O-Cl distance is shorter than 3.21 Å, the sum of ionic radii⁷² of Cl^- and O^{2-} ⁷². Similarly the H₂O-OH₂ distance for H-bonding would need to be less than 2.80 Å.

3.4. Structure analyses of $(\text{NH}_4)_2\text{MoCl}_5\text{H}_2\text{O}$, $\text{Rb}_2\text{MoCl}_5\text{H}_2\text{O}$ and $\text{Rb}_2\text{FeCl}_5\text{H}_2\text{O}$

A comparison of the X-ray powder data suggests that these three compounds are isomorphous with $\text{K}_2[\text{MoCl}_5\text{H}_2\text{O}]$. Structure analyses confirmed this. Models for each of the three compounds were derived from that of $\text{K}_2[\text{MoCl}_5\text{H}_2\text{O}]$, and the structure refinements carried out by full-matrix least-squares methods. The final R-factors were 9.5%, 10.4% and 7.9% for $(\text{NH}_4)_2\text{MoCl}_5\text{H}_2\text{O}$, $\text{Rb}_2\text{MoCl}_5\text{H}_2\text{O}$ and $\text{Rb}_2\text{FeCl}_5\text{H}_2\text{O}$ respectively. A comparison of atomic coordinates and thermal parameters for these three compounds and for $\text{K}_2[\text{MoCl}_5\text{H}_2\text{O}]$ is shown in Table 3.3. Lists of final F_{obs} and F_{calc} are given in Appendix 3 Tables A.3.5-3.7 for the three

compounds. For convenience of presentation relevant distances and bond angles are included in the later discussion segment in Table 3.6.

The standard deviations attached to atomic coordinates, thermal parameters, bond lengths and angles (Tables 3.3, 3.4, 3.6, and 3.7) are a measure of the consistency of the data set and do not take into account errors inherent in intensity measurement or in the measurement of unit cell dimensions. (See discussion Section 1.5).

3.5. Structure Analyses of $\text{Cs}_2\text{MoCl}_5\text{H}_2\text{O}$ and $\text{Cs}_2\text{FeCl}_5\text{H}_2\text{O}$

The systematic absences observed in the Weissenberg photographs of both $\text{Cs}_2\text{MoCl}_5\text{H}_2\text{O}$ and $\text{Cs}_2\text{FeCl}_5\text{H}_2\text{O}$ are for: $\underline{hk\ell} : \underline{h+k}$ odd; $\underline{h0\ell} : \underline{\ell}$ odd.

The two orthorhombic space groups corresponding to this absence pattern are Cmcm or $\text{Cmc}2_1$. The centrosymmetric space group Cmcm was chosen and later shown to be correct. The X-ray powder data suggests that both compounds are isomorphous with $\text{Cs}_2[\text{RuCl}_5\text{H}_2\text{O}]$. To check this, a three-dimensional Patterson function for $\text{Cs}_2\text{MoCl}_5\text{H}_2\text{O}$ was calculated in Pmmm , the Patterson group for this orthorhombic space group. The analysis of this function was carried out in a manner similar to that described above for $\text{K}_2[\text{MoCl}_5\text{H}_2\text{O}]$. (Section 3.3). The basic features of the structure were deduced from a study of the relevant Harker lines and planes. Idealized plots of Patterson sections with $x = 0$ and $x = \frac{1}{4}$ are shown as Figs. 3.4 and 3.5. The allocation of interatomic vectors is marked on these maps.

Based on models derived from the Patterson function, the complete structures of both compounds were determined from difference Fourier maps, and refined by the full-matrix least-squares method to residual R-factors of 9.6% and 8.3%, for $\text{Cs}_2\text{MoCl}_5\text{H}_2\text{O}$ and $\text{Cs}_2\text{FeCl}_5\text{H}_2\text{O}$ respectively. However, when the coordinates of the oxygen atoms were included in the least-squares refinement cycles the resulting positions gave holes on the difference Fourier maps, and also gave peak locations which suggested moving

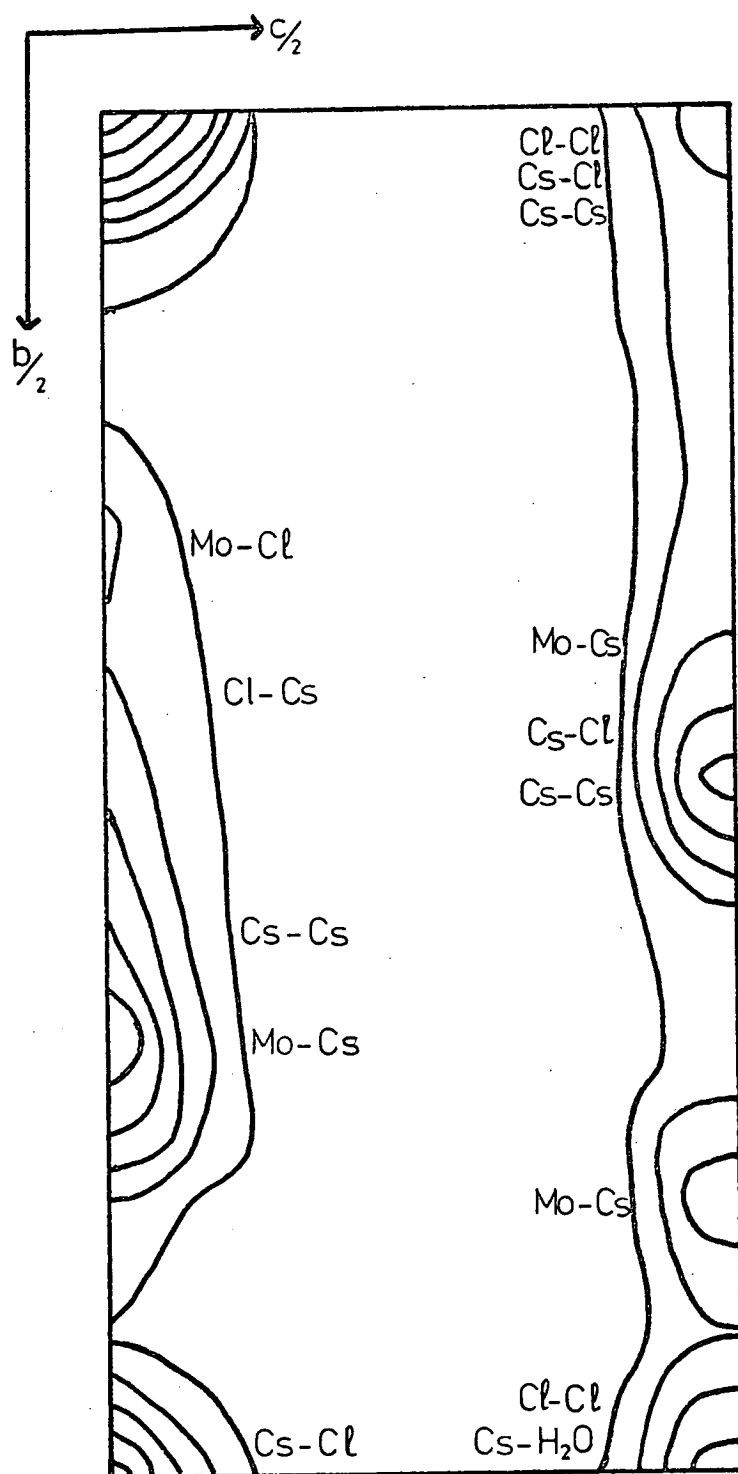


Fig.3.4 Patterson section $x=0$ $\text{Cs}_2\text{MoCl}_5\text{H}_2\text{O}$
Showing assigned interatomic vectors

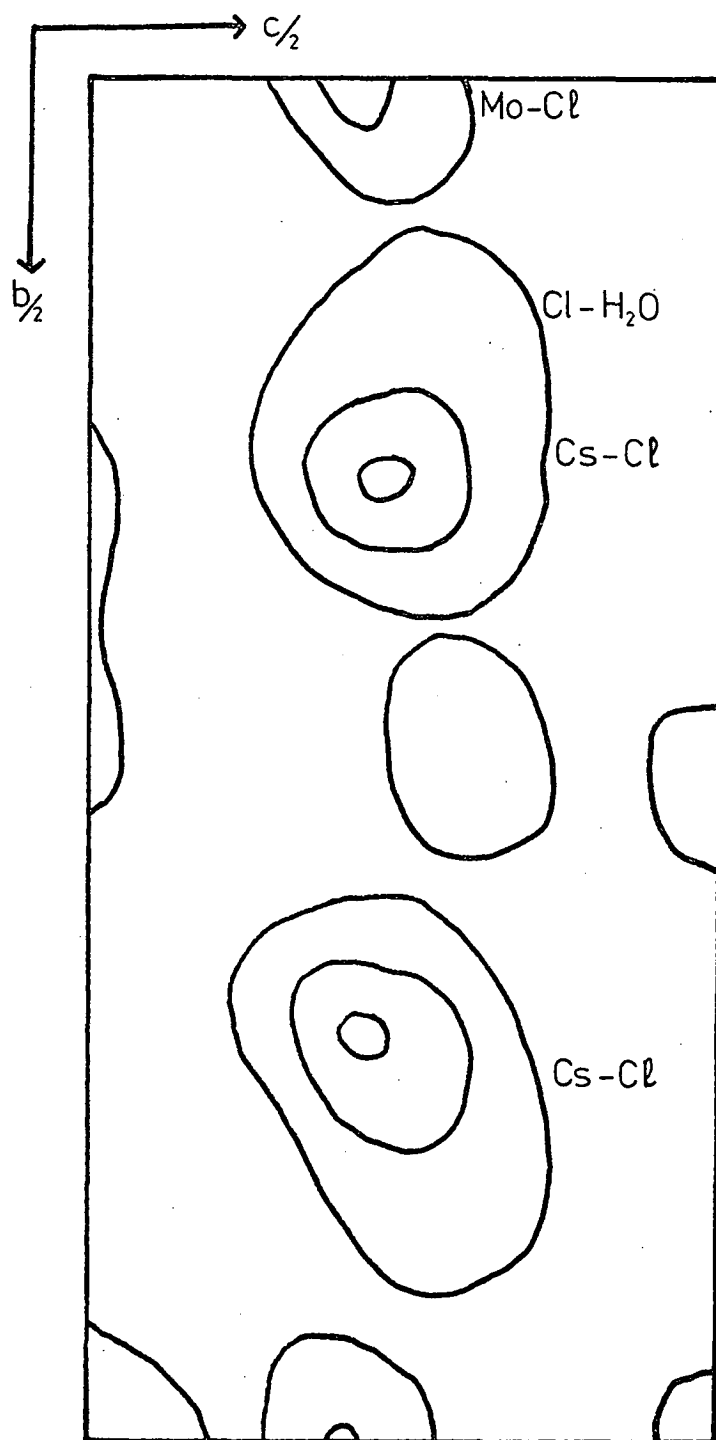


Fig.3.5 Patterson section $x = \frac{1}{4}$ $\text{Cs}_2\text{MoCl}_5\text{H}_2\text{O}$ showing assigned interatomic vectors

the atoms back towards their original positions. To overcome this problem the oxygen atom positions were fixed from accurate measurement of peak centres on the difference Fourier maps and only the temperature factors of these atoms included in the refinement cycles. As the shifts in parameters at this stage were less than the standard deviations, and as final Fourier and difference Fourier maps showed no anomalies, the structure refinements were concluded. At this stage the R-factors were the same as mentioned above.

Powder and crystallographic data for both compounds have been presented above in Tables 3.1 and 3.2 (Section 3.2). A comparison of atomic and thermal parameters for these two compounds is shown in Table 3.4. Lists of final F_{obs} and F_{calc} are given in Appendix 3 Tables A3.8 and A3.9. Relevant bond lengths and angles are included in the later discussion segment (Table 3.7).

Description of Structure of $\text{Cs}_2[\text{MoCl}_5\text{H}_2\text{O}]$ and $\text{Cs}_2[\text{FeCl}_5\text{H}_2\text{O}]$

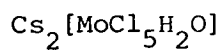
To illustrate these two isomorphous structures, that of $\text{Cs}_2[\text{MoCl}_5\text{H}_2\text{O}]$ viewed in projection along [100] is shown in Fig. 3.6. The structure is isomorphous with that found for $\text{Cs}_2[\text{RuCl}_5\text{H}_2\text{O}]$. The choice here of space group Cmc \bar{m} in preference to Am \bar{m} reported for $\text{Cs}_2[\text{RuCl}_5\text{H}_2\text{O}]$ ⁶⁸ was made to conform with the orientation used by the International Tables for X-Ray Crystallography Volume 1⁹, although both space groups are the same.

The central Mo atoms of the distorted octahedral $[\text{MoCl}_5\text{H}_2\text{O}]^{2-}$ ion are located in a four-fold special position at $(0, y, 1/4)$, $(0, \bar{y}, 3/4)$, $(1/2, 1/2+y, 1/4)$ and $(1/2, 1/2-y, 3/4)$. The octahedra are oriented with the trans Cl-Mo-H₂O direction lying in the planes with $x = 0$ and $x = 1/2$ and at right angles to the c axis. The remaining four chlorines occupy a general sixteen-fold (x, y, z) position and lie just above and below planes with $x = 1/4$ and $x = 3/4$. The central Mo atom lies out of the plane of the four chlorine atoms which themselves form a rectangle rather than a square. Both the Cl(1)-Mo-Cl(2)

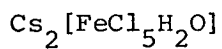
TABLE 3.4

Atomic Coordinates and Isotropic Temperature Factors

(Standard deviations in parenthesis)



Atom	Position	x	y	z	B
Mo	4(c)	0	0.1175(1)	0.25	1.78(3)
Cs(1)	4(c)	0	0.4711(1)	0.25	3.25(4)
Cs(2)	4(c)	0	0.7540(1)	0.25	3.68(5)
Cl(1)	4(c)	0	0.2516(4)	0.25	2.91(16)
Cl(2)	16(h)	0.2261(5)	0.1122(2)	0.4620(3)	4.17(7)
O(H ₂ O)	4(c)	0	-0.0070	0.25	5.48(63)



Atom	Position	x	y	z	B
Fe	4(c)	0	0.1216(2)	0.25	1.54(6)
Cs(1)	4(c)	0	0.4704(1)	0.25	1.60(3)
Cs(2)	4(c)	0	0.7541(1)	0.25	2.20(4)
Cl(1)	4(c)	0	0.2562(4)	0.25	3.01(19)
Cl(2)	16(h)	0.2229(5)	0.1116(1)	0.4575(2)	2.06(5)
O(H ₂ O)	4(c)	0	-0.0010	0.25	4.88(52)

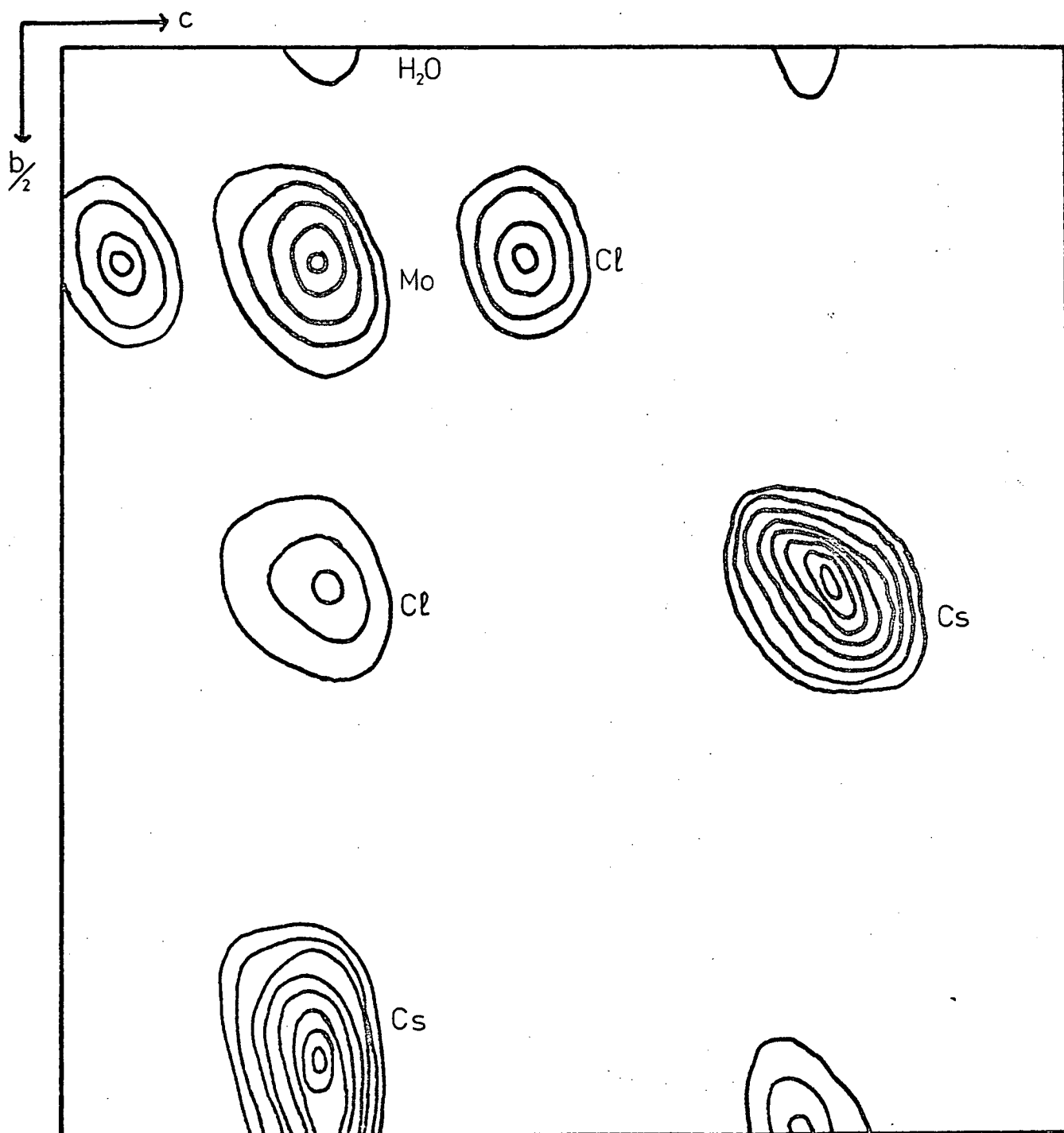


Fig.3.6 Fourier projection [100] from $x = 0$ to $x = \frac{1}{4}$ for $\text{Cs}_2[\text{MoCl}_5\text{H}_2\text{O}]$

bond angles of 92.2° and the $\text{Cl}(2)\text{-Mo-OH}_2$ of 87.8° are distorted from 90° by appreciable amounts, giving rise to a point symmetry of 2mm for the Mo rather than the symmetrical 4mm point group. This contrasts with the structure of for example, $\text{K}_2[\text{MoCl}_5\text{H}_2\text{O}]$ where the Mo lies at the midpoint of a line between two chlorines rather than on the line between chlorine and the water molecule. Also the four chlorines of $\text{K}_2[\text{MoCl}_5\text{H}_2\text{O}]$ do not lie in a plane as in $\text{Cs}_2[\text{MoCl}_5\text{H}_2\text{O}]$ and the point group of the molybdenum atom is 1 rather than 2mm .

The Cs^+ ions occupy two four-fold special positions of the type $(0,y,1/4)$ and link the octahedral with strong electrostatic attraction both in the plane with $x = 0$ and between octahedral units in planes with $x = 0$ and $x = \frac{1}{2}$. Again there is no evidence for H-bonding between ligands of different octahedra; the distance of closest approach of $\text{Cl-H}_2\text{O} = 3.419 \text{ \AA}$ and $\text{H}_2\text{O-H}_2\text{O} = 4.065 \text{ \AA}$ being outside the expected hydrogen-bonded limits.

3.6. Discussion

Crystallographic data for the twelve compounds of type $\text{A}_2[\text{MCl}_5\text{H}_2\text{O}]$ whose structures have been determined by three-dimensional X-ray analysis have been given above in Table 3.2 (page 51).

There is an expected clear pattern to be observed in the unit cell dimensions. As the central metal ion increases in size so does the volume of the unit cell. In a similar manner the unit cell volume increases as the size of the cation increases.

On the basis of the X-ray crystal structure evidence now available, both from single crystal and from powder data, compounds of the type $\text{A}_2^{\text{I}}[\text{M}^{\text{III}}\text{X}_5\text{H}_2\text{O}]$ can be classified as belonging to either the Pnma , $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ type⁶⁴ or to the Cmcm , $\text{Cs}_2[\text{RuCl}_5\text{H}_2\text{O}]$ type⁶⁸. These are listed in Table 3.5. Podmore⁶¹ has suggested that the changeover point from one structural type to the other is related to the size of the M^{3+} central ion. The same author suggests

TABLE 3.5

Classification of $A_2MX_5H_2O$ Compounds

[Rh(NH ₃) ₅ Cl]Cl ₂ type			Cs ₂ [RuCl ₅ H ₂ O] type		
Compound	X-ray data	Reference	Compound	X-ray data	Reference
$A_2^I TiCl_5H_2O$ (A = K ⁺ , NH ₄ ⁺ , Rb ⁺)	Powder	61	Cs ₂ TiCl ₅ H ₂ O	Powder	61
$A_2^I Vx_5H_2O$ X = Cl, Br (A = K ⁺ , NH ₄ ⁺ , Rb ⁺)	Powder	61	Cs ₂ VCl ₅ H ₂ O	Powder	61
$A_2^I Crx_5H_2O$ (A = K ⁺ , NH ₄ ⁺ , Rb ⁺) X = Cl, Br	Powder	61	Cs ₂ VBr ₅ H ₂ O	Powder	61
$K_2FeCl_5H_2O$	Single Crystal	62	Cs ₂ CrCl ₅ H ₂ O	Powder	61
$(NH_4)_2FeCl_5H_2O$	Single Crystal	63	Cs ₂ CrBr ₅ H ₂ O	Powder	61
$(Rb_2)FeCl_5H_2O$	Single Crystal	This work	Cs ₂ FeCl ₅ H ₂ O	Single Crystal	This work
$A_2^I FeBr_5H_2O$ (A = K ⁺ , NH ₄ ⁺ , Rb ⁺)	Powder	61	Cs ₂ FeBr ₅ H ₂ O	Powder	61
$K_2MoCl_5H_2O$	Single Crystal	This work	Cs ₂ MoCl ₅ H ₂ O	Single Crystal	This work
$(NH_4)_2MoCl_5H_2O$	Single Crystal	This work			
$RbMoCl_5H_2O$	Single Crystal	This work			
$A_2^I MoBr_5H_2O$ (A = K, NH ₄ , Rb)	Powder	61	Cs ₂ MoBr ₅ H ₂ O	Powder	61
$K_2RuCl_5H_2O$	Single Crystal	65	Cs ₂ RuCl ₅ H ₂ O	Single Crystal	68
Cs ₂ TlCl ₅ H ₂ O	Single Crystal	67			
$(NH_4)_2InCl_5H_2O$	Single Crystal	66			

that there is a limiting central metal M^{3+} ionic radius above which the Cs^+ salts revert to the $[Rh(NH_3)_5Cl]Cl_2$ structure because of the more favourable crystal packing arrangements. In the one caesium salt, $Cs_2[TlCl_5H_2O]$, which has been shown⁶⁷ to crystallize with the Pnma symmetry, the ionic radius of Tl^{3+} (1.05 \AA)⁷² is much greater than the radii of the M^{3+} in transition metal compounds studied. For example, the ionic radius of Fe^{3+} is 0.628 \AA ⁷². If it were possible to prepare crystalline $Cs_2[InCl_5H_2O]$, (In ionic radius = 0.714 \AA)⁷² classification of this structure into either the Pnma or Cmcmm symmetry would help towards the solution of the problem. Podmore⁶¹ suggests that the structure of $Cs_2[GaCl_5H_2O]$ might also lie somewhere near the changeover borderline.

For the compounds which crystallize with space group Pnma a comparison of the major bond lengths and angles within the complex ions and some short contact distances in the structures are given in Table 3.6. Similar data for the three compounds crystallizing in space group Cmcmm are given in Table 3.7.

Neglecting the high $M-OH_2$ bond length in $K_2[MoCl_5H_2O]$ the average bond lengths calculated over all the Mo and Fe structures reported gives:

$$\begin{aligned} Mo-Cl &= 2.42 \pm 0.02 \text{ \AA}; \quad Fe-Cl = 2.39 \pm 0.05 \text{ \AA}; \quad Mo-OH_2 = 2.17 \pm 0.01 \text{ \AA}; \\ Fe-OH_2 &= 2.09 \pm 0.04 \text{ \AA}. \end{aligned}$$

The average Fe-Cl distance lies midway between reported values of $Fe-Cl = 2.48 \text{ \AA}$ in anhydrous $FeCl_3$ and $Fe-Cl = 2.30 \text{ \AA}$ in $[FeCl_2(H_2O)_4]Cl \cdot 2H_2O$ ⁷³. This is probably to be expected as there is a decrease in octahedral symmetry around the central iron atom from $FeCl_3$ through $[FeCl_5H_2O]^{2-}$ to $[FeCl_2(H_2O)_4]^+$.

The $Fe-OH_2$ distance of 2.09 \AA is within the limits, the same as that found in $[FeCl_2(H_2O)_4]Cl \cdot 2H_2O$ ⁷³ where $Fe-OH_2 = 2.07 \text{ \AA}$.

A comparison of the symmetry of the complex ions in $Rb_2[MoCl_5H_2O]$ and $Cs_2[MoCl_5H_2O]$ is shown as Fig. 3.7. As can be seen from these diagrams the distortion of both these complex ions is approximately the same. The

TABLE 3.6

Bond Lengths (Å) and Bond Angles (degrees)

(Standard deviations in parenthesis)

[M = Mo, Fe, Ru, In]

[A = K, NH₄, Rb, Cs]

	K ₂ [MoCl ₅ H ₂ O]	(NH ₄) ₂ [MoCl ₅ H ₂ O]	Rb ₂ [MoCl ₅ H ₂ O]	K ₂ [FeCl ₅ H ₂ O] ⁶²	(NH ₄) ₂ [FeCl ₅ H ₂ O] ⁶³
M-Cl (1)	2.488 (2)	2.450 (2)	2.491 (3)	2.50	2.35
M-Cl (2)	2.381 (2)	2.425 (2)	2.415 (2)	2.39	2.39
M-Cl (3)	2.396 (2)	2.413 (2)	2.436 (3)	2.39	2.39
M-Cl (4)	2.384 (6)	2.439 (1)	2.412 (5)	2.45	2.41
Av. M-Cl	2.407 (42)	2.433 (20)	2.433 (58)	2.44	2.39
M-OH ₂	2.26 (5)	2.167 (4)	2.183 (5)	2.05	2.08
A-Cl (1)	3.314 (2)	3.372 (3)	3.311 (1)	3.50	
A-Cl (2)	3.300 (2)	3.332 (4)	3.374 (2)	3.35	
A-Cl (3)	3.246 (3)	3.262 (4)	3.338 (2)	3.40	
A-Cl (4)	3.271 (3)	3.447 (2)	3.425 (2)	3.45	
A-OH ₂	3.940 (5)	3.893 (6)	3.955 (4)	3.85	

	Rb ₂ [FeCl ₅ H ₂ O]	K ₂ [RuCl ₅ H ₂ O] ⁶⁵	(NH ₄) ₂ (InCl ₅ H ₂ O) ⁶⁶	Cs ₂ [TiCl ₅ H ₂ O] ⁶⁷
M-Cl (1)	2.404 (3)	2.34	2.52	2.54
M-Cl (2)	2.298 (2)	2.31	2.71	2.52
M-Cl (3)	2.356 (3)	2.33	2.60	2.51
M-Cl (4)	2.401 (1)	2.50	2.54	2.55
Av. M-Cl	2.372 (74)	2.40	2.58	2.53
M-OH ₂	2.108 (6)	2.12	2.23	2.29
A-Cl (1)	3.317 (1)			3.42
A-Cl (2)	3.372 (2)			3.59
A-Cl (3)	3.300 (2)			3.63
A-Cl (4)	3.429 (2)			3.48
A-OH ₂	3.951 (6)			4.02

TABLE 3.6 (Cont.)

	$K_2[MoCl_5H_2O]$	$(NH_4)_2[MoCl_5H_2O]$	$Rb_2[MoCl_5H_2O]$	$Rb_2[FeCl_5H_2O]$
< Cl(1)-M-OH ₂	87.8(1)	87.6(1)	87.5(1)	89.4(2)
< Cl(2)-M-OH ₂	178.0(2)	177.6(1)	179.2(1)	179.3(2)
< Cl(3)-M-OH ₂	90.4(2)	92.8(2)	89.4(2)	92.4(2)
< Cl(4)-M-OH ₂	88.0(2)	87.3(1)	87.1(2)	85.8(2)
< Cl(1)-M-Cl(2)	90.1(1)	90.0(1)	91.8(1)	89.9(1)
< Cl(1)-M-Cl(3)	178.5(1)	179.6(1)	179.8(1)	179.5(1)
< Cl(1)-M-Cl(4)	88.2(1)	89.5(1)	88.9(1)	89.1(1)
< Cl(2)-M-Cl(3)	91.4(1)	89.6(1)	88.4(1)	91.6(1)
< Cl(2)-M-Cl(4)	91.9(2)	92.7(1)	92.9(1)	94.1(1)
< Cl(3)-M-Cl(4)	91.7(2)	90.5(1)	91.1(1)	90.8(1)

TABLE 3.7

Bond Lengths (Å) and Bond Angles (degrees)

(Standard deviations in parenthesis)

[M = Mo, Fe, Ru]

	$Cs_2[MoCl_5H_2O]$	$Cs_2[FeCl_5H_2O]$	$Cs_2[RuCl_5H_2O]$ ⁶⁸
M-Cl(1)	2.339(2)	2.329(2)	2.311(8)
M-4Cl(2)	2.416(2)	2.364(2)	2.353(4)
M-OH ₂	2.170(1)	2.121(1)	2.104(28)
M-Cl(Av)	2.401(62)	2.357(28)	2.34
Cs(1)-4Cl(2)	3.432(2)	3.442(2)	3.408(4)
Cs(1)-OH ₂	3.765(1)	3.750(1)	3.720(3)
Cs(1)-Cl(1)	3.828(2)	3.707(2)	3.848(8)
Cs(2)-4Cl(2)	3.645(2)	3.624(2)	3.619(4)
Cs(2)-Cl(1)	3.745(1)	3.718(1)	3.701(2)
Cs(2)-OH ₂	4.168(1)	4.238(1)	4.153(28)
Cl(1)-4Cl(2)	3.426(2)	3.437(2)	3.347(7)
Cl(2)-OH ₂	3.185(2)	3.059(2)	3.109(18)
Cl(2)-Cl(2)	3.387(5)	3.314(5)	3.289(8)
Cl(2)-Cl(2)	3.440(3)	3.353(2)	3.363(8)
< Cl(2)-M-OH ₂	87.8(1)	85.8(1)	88.3(1)
< Cl(2)-M-Cl(2)	89.0(1)	89.0(1)	91.2(2)
< Cl(2)-M-Cl(2)	90.8(1)	90.4(1)	88.7(2)
< Cl(2)-M-Cl(1)	92.2(1)	94.2(1)	91.7(1)

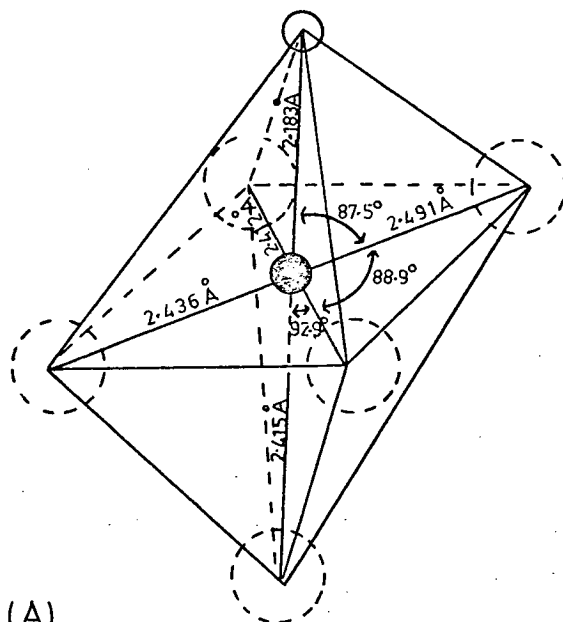


Fig.3.7 (A)

$[\text{MoCl}_5\text{H}_2\text{O}]^{2-}$ configuration in $\text{Rb}_2[\text{MoCl}_5\text{H}_2\text{O}]$

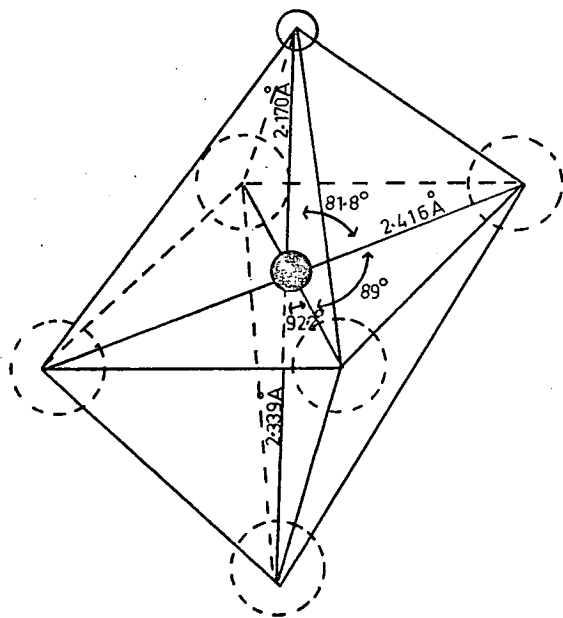
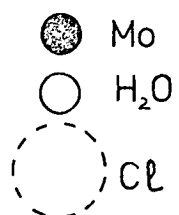


Fig.3.7(B)

$[\text{MoCl}_5\text{H}_2\text{O}]^{2-}$ configuration in $\text{Cs}_2[\text{MoCl}_5\text{H}_2\text{O}]$



$[\text{MCl}_5\text{H}_2\text{O}]^{2-}$ structural type may thus be regarded as a deformed octahedral structure. This accounts for the lower symmetry of these compounds by comparison to the cubic symmetry shown, for example, by K_2PtCl_6 where the complex ion has regular octahedral symmetry.

As mentioned in Section 3.1 far infrared spectra of these compounds showed definite trends in the M-O and M-Cl stretching frequencies in comparative series of these compounds⁶¹. It was thought that these variations might occur in systematic fashion and could be a result of packing considerations caused by different sized atoms. Also considerations of H-bonding could not be ruled out.

Within the accuracy of the structure studies reported in this work, however, it was found that the M-Cl and M-OH₂ bond lengths for the same central metal were approximately the same.

N.q.r. studies show several anomalies. For instance, $\text{Rb}_2[\text{FeCl}_5\text{H}_2\text{O}]$ and $\text{Rb}_2[\text{CrCl}_5\text{H}_2\text{O}]$ exhibit ³⁵Cl n.q.r. frequencies at temperatures ranging from 77°K to 298°K, whereas such frequencies were not observed in $\text{Rb}_2[\text{MoCl}_5\text{H}_2\text{O}]$ even at low temperatures⁶¹. In compounds of the $\text{Cs}_2[\text{RuCl}_5\text{H}_2\text{O}]$ structural type ³⁵Cl n.q.r. frequencies observed at 298°K for $\text{Cs}_2[\text{CrCl}_5\text{H}_2\text{O}]$ and $\text{Cs}_2[\text{MoCl}_5\text{H}_2\text{O}]$ were not observed for $\text{Cs}_2[\text{FeCl}_5\text{H}_2\text{O}]$ ⁶¹. It is possible that M-Cl bond lengths might vary because of different degrees of hydrogen-bonding between molecules, or that these n.q.r. anomalies might simply be due to the different size of the metal ions causing differences in the overall crystal lattice. On the other hand, the n.q.r. data collecting process may suffer from problems such as low signal-noise ratio which might make consistent data difficult to obtain. However, the X-ray structural evidence discussed above shows no significantly different degrees of hydrogen-bonding in these compounds and does not show any variations in bond-lengths to account for the differences in n.q.r. spectra.

Chapter 4

Crystal Structures of Vanadium(III) Aqua Chloro Complexes

I. $\text{Cs}_2\text{VCl}_5 \cdot 4\text{H}_2\text{O}$ and $\text{Cs}_2\text{VBr}_5 \cdot 4\text{H}_2\text{O}$

4.1. Introduction

Of particular interest in the study of the coordination chemistry of vanadium(III) is a series of aqua chloro complexes which have been isolated by several workers⁷⁴⁻⁸¹. Recently Podmore and Smith⁷⁰ of these laboratories have reported spectral, magnetic susceptibility and some X-ray powder data on a range of such compounds. Their report deals in particular with a group of "green" compounds of empirical formulae $\text{VX}_3 \cdot 6\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$), $\text{RbVCl}_4 \cdot 6\text{H}_2\text{O}$, and $\text{Cs}_2\text{VX}_5 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}$ or Br ; $n = 4$ or 5).

Reflectance spectra in the visible region were assigned by Podmore and Smith⁷⁰, and others^{77,82}, on the basis of an octahedral ligand field, to suggest the presence of $[\text{VX}_2(\text{H}_2\text{O})_4]^+$ complex ions in these compounds.

Infrared spectra in the region $4000\text{--}270\text{ cm}^{-1}$ showed only one band in the expected V-X ($\text{X} = \text{Cl}$ or Br) stretching frequency range for compounds containing $[\text{VX}_2(\text{H}_2\text{O})_4]^+$ ions. This was interpreted as being evidence for trans complex ions. By comparison, Podmore and Smith have found two measurable M-Cl stretching frequencies for a related compound $[\text{VCl}_4(\text{CH}_3\text{COOH})_2]$, and from this have postulated a cis configuration of the acetic acid ligands.

For the "green" V(III) complexes studied by Podmore and Smith the magnetic moments recorded at room temperature are close to the spin-only value expected for octahedral coordination. For the range of V(III) compounds reported they also found that magnetic moments varied with temperature in the order $[\text{VCl}_2(\text{H}_2\text{O})_4]^+ < [\text{VCl}_5(\text{H}_2\text{O})]^{2-} < [\text{VCl}_6]^{3-}$, suggesting a larger ground state splitting for the $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ compounds. This would indicate a greater distortion from the cubic field for this type of compound than for the others.

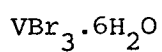
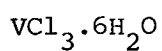
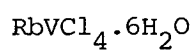
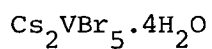
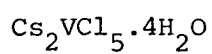
Similar compounds of other first row transition metals have also been reported by other workers. Podmore⁶¹ has reviewed the literature up to 1973. Probably the most significant results in this area are those of X-ray diffraction studies. The compounds $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ have been shown to have crystal structures which contain the complex ions $[\text{FeCl}_2(\text{H}_2\text{O})_4]^+{}^{83}$ and $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+{}^{84,85}$ respectively. This is in contrast to the structure of the non-transition metal compound $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, which has been shown⁸⁶ to consist of $[\text{Gd}(\text{H}_2\text{O})_6]^{3+}$ and Cl^- ions. Compounds of similar stoichiometry but with the central metal in the 2+ state have also been studied. Two of these compounds, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ⁸⁷, and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ⁸⁸ crystallize with trans- $[\text{MCl}_2(\text{H}_2\text{O})_4]^\circ$ (M = Co or Ni) units in their crystal lattices. Another similar compound but of a non-transition metal, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ⁸⁹, however, contains $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ complex ions and Cl^- ions. Thus it is of particular interest to identify the type of complex ion present in the "green" V(III) complexes discussed above.

The best method of effectively clarifying these structural problems associated with the V(III) compounds is by X-ray crystal structure analysis. In the field of V(III) chemistry a survey of the literature to March 1973 reveals that, apart from single crystal X-ray studies reported on four coordination compounds of vanadium(III), $\text{K}_3[\text{V}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ ^{90,91}, $\text{V}[\text{PS}_2(\text{OEt})_2]_3$ ⁹², $\text{VCl}_3(\text{NMe}_2)_3$ ⁹³ and $[(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CF}_3\text{COO})_2]_2$ ⁹⁴; there is very little X-ray data, other than that obtained by powder diffraction for simple V(III) compounds. The results of this survey are listed in tabular form in Appendix 4.

In order, therefore, to obtain more structural information about the "green" aqua halides of vanadium(III), single crystal X-ray structure analyses were carried out on five compounds whose overall stoichiometry can be expressed as shown in Table 4.1. In this chapter the structures of the two caesium compounds, $\text{Cs}_2\text{VCl}_5 \cdot 4\text{H}_2\text{O}$ and $\text{Cs}_2\text{VBr}_5 \cdot 4\text{H}_2\text{O}$ will be presented. The following two chapters will deal with similar reports on the other three

TABLE 4.1

Overall Stoichiometry of V(III) Compounds Studied



compounds shown in Table 4.1. A subsequent chapter will be devoted to a comparative discussion of the five V(III) crystal structures reported herein.

4.2. The Crystal Structure of $\text{Cs}_2\text{VCl}_5 \cdot 4\text{H}_2\text{O}$

4.2.1. Experimental

Preparation - Crystal Selection

The sample used was prepared by Podmore of this Department⁶¹. The green crystalline compound was obtained from an aqueous solution containing caesium chloride and vanadium(III) chloride, by saturating with hydrogen chloride at room temperature. The needle shaped crystals were extremely sensitive to moisture and to oxygen, and this made the mounting of single crystals difficult. It was possible, however, to handle the compound in air for a few minutes, thus allowing suitable crystals to be selected with the aid of a binocular microscope. The crystals were then sealed into previously dried capillaries. This proved unsuccessful because the crystals decomposed rapidly, probably by reacting with oxygen from the air in the capillaries.

The next step was to coat selected crystals with inert protective materials such as nujol, paraffin oil, vacuum grease and various commercial preparations. The coated crystals were then sealed in capillary tubes. This was partially successful but in each case after one or two days the crystals decomposed, thus making data collection by normal photographic methods unsatisfactory.

The crystal finally used for X-ray data collection was one of several transferred into a dried capillary tube drawn from the side of the main reaction vessel. The operation was carried out under nitrogen atmosphere on a vacuum line. Many attempts were required before a suitable single crystal lodged in the capillary tube at an appropriate angle, and sufficiently separated from its neighbours. This crystal had approximate dimensions of 0.2 x 0.1 x 0.1 mm.

X-ray data collection

Cell parameters were initially obtained from oscillation and equi-inclination Weissenberg X-ray photographs of this single crystal. Further refinement of these parameters was carried out by least squares methods on X-ray powder data (Table 4.2) collected from a Philips powder diffractometer using Cu K_α radiation and KCl as an internal calibrant. The lattice parameters are given in Table 4.3. This powder work was carried out jointly by Podmore⁶¹ and the author.

The density reported elsewhere⁹⁵ was verified by the gradient tube method described in Appendix 2. From this and the cell volume, it was calculated that the unit cell contained two formula units ($z = 2$) of $\text{Cs}_2\text{VCl}_5 \cdot 4\text{H}_2\text{O}$ molecules per unit cell.

Trial zero level equi-inclination Weissenberg X-ray photographs taken with Cu K_α radiation showed the diffraction spots to be of reasonably regular shape. Because of this and because of the difficulty in mounting a stable single crystal, non-integrated data were collected for several further levels by the Weissenberg technique on 4-film packs as discussed in Section 1.3. These photographs were taken about the monoclinic b -axis for the four levels hnl ($n = 0-3$), giving a total of 243 observed reflections. This number could have been increased by data collection of levels with $k > 3$ and about another axis. As will be shown later, however, these 243 observed reflections provided sufficient data for structure determination and refinement. (See Section 4.2.2). This together with the difficulties with crystal stability was considered sufficient reason for limiting the data collection. Also attempts to photograph level $h4l$ showed only a few reflections of very poor resolution. The photographs of the various layers were taken over periods ranging from 48 hours for the zero $h0l$ level to 57 hours for the third $h3l$ level. Using these exposure times the most intense reflections for each level fell into a measurable range on the fourth

TABLE 4.2

X-Ray Powder Data

61

$\text{Cs}_2\text{VCl}_5 \cdot 4\text{H}_2\text{O}$		$\text{Cs}_2\text{VBr}_5 \cdot 4\text{H}_2\text{O}$	
$\sin^2 \theta_{\text{obs.}}$	$\sin^2 \theta_{\text{calc.}}$	$\sin^2 \theta_{\text{obs.}}$	$\sin^2 \theta_{\text{calc.}}$
81.7 m	81.9	120.8 w	121.3
129.7 m	130.7	313.3 m	313.4
153.4 vw	154.3	450.2 m	454.9
326.8 s	327.8	484.8 w	485.4
339.3 s	340.0	515.2 m	514.2
383.3 vw	383.2	615.1 s	615.1
487.9 m	488.1	639.7 s	639.9
522.2 vs	522.8	668.6 m	666.7
558.1 w	558.2	834.0 m	835.7
574.2 w	575.1	868.9 vw	876.4
621.9 m	622.4	900.2 vw	891.9
667.7 s	667.8	964.7 vw	959.0
687.8 m	687.9	1067.5 w	1067.6
705.2 vw	704.4	1102.8 w	1103.7
720.1 m	721.4	1255.8 m	1253.5
739.1 w	737.5	1289.0 w	1294.3
756.0 vw	757.3	1338.5 vw	1334.0
776.9 vw	776.8	1371.3 vw	1374.3
896.7 m	899.0	1873.1 vw	1869.0
1037.5 vw	1037.8	1933.4 m	1937.1
1087.0 vw	1086.0	1943.1 m	1941.4
1112.6 w	1110.6		
1164.2 w	1159.4		
1206.5 vw	1208.5		
1261.0 vw	1265.0		
1311.9 w	1311.1		
1342.1 w	1343.9		
1367.7 w	1367.4		
1390.0 vw	1389.9		
1438.6 vw	1440.0		
1479.9 vw	1480.0		
1524.9 vw	1522.5		
1581.7 vw	1580.9		

TABLE 4.3

Crystallographic Data

	$\text{Cs}_2\text{VCl}_5 \cdot 4\text{H}_2\text{O}$	$\text{Cs}_2\text{VBr}_5 \cdot 4\text{H}_2\text{O}^{61}$
a	$17.745 \pm 0.008 \text{ \AA}$	$18.484 \pm 0.009 \text{ \AA}$
b	$6.183 \pm 0.005 \text{ \AA}$	$6.423 \pm 0.005 \text{ \AA}$
c	$7.019 \pm 0.005 \text{ \AA}$	$7.266 \pm 0.006 \text{ \AA}$
β	$106.4 \pm 0.5^\circ$	$106.1 \pm 0.5^\circ$
z	2	2
$d_{\text{obs}}^{\text{calc}}$	2.50 g/cc	3.20 g/cc
d_{obs}	2.54 g/cc	3.16 g/cc
Systematic Absences	$\underline{hk\ell}: \underline{h+k} = 2n+1$	$\underline{hk\ell}: \underline{h+k} = 2n+1$
Space Group	Monoclinic C2/m	C2/m
Axis of data Collection	\underline{b}	\underline{b}
Observed Reflections	243	511

film of the packs. It was also found that the increase of exposure times by about three hours per successive level helped place the data from various layers on a reasonably close overall scale. The intensities of the reflections observed were estimated visually with a standard scale and were corrected for Lorentz and polarisation factors. No correction was made for absorption. The optimum thickness calculated for this compound is 0.04 mm. In neglecting absorption corrections it is possible, therefore, that there would be some slight decrease in the accuracy of measurements of intensity data. (See also Section 1.5.1).

Inspection of the equi-inclination Weissenberg photographs revealed the compound to be monoclinic, and that reflections with $h+k$ odd were systematically absent. The space groups corresponding to these observations are $C2/m$, Cm or $C2^9$. In accordance with general crystallographic practise the centrosymmetric $C2/m$ was chosen as the most likely space group. The subsequent structure determination confirmed this choice.

4.2.2. Structure Determination and Refinement

A three-dimensional Patterson function was calculated in space group $C2/m$, which is also the Patterson space group. Sections were calculated along the b -axis at intervals of $1/40$ for sections 0-20. A plot of the relevant Harker plane (xOz) is shown as Fig. 4.1, with dimensions $\underline{a}/2 \times \underline{c}$.

The main Patterson vector information is contained in this Harker plane and in the Harker line (OyO). In fact, there are no significant peaks outside the plane with $y = 0$ except in the symmetry related plane with $y = \frac{1}{2}$, and this was interpreted to mean that most of the scattering material of the real cell is likewise located in the planes with $y = 0$ and $y = \frac{1}{2}$. This is confirmed by the fact that the only peak on the Harker line (OyO) occurs at the origin.

With $\underline{z} = 2$ it was possible to fix the two vanadium atoms in the unit

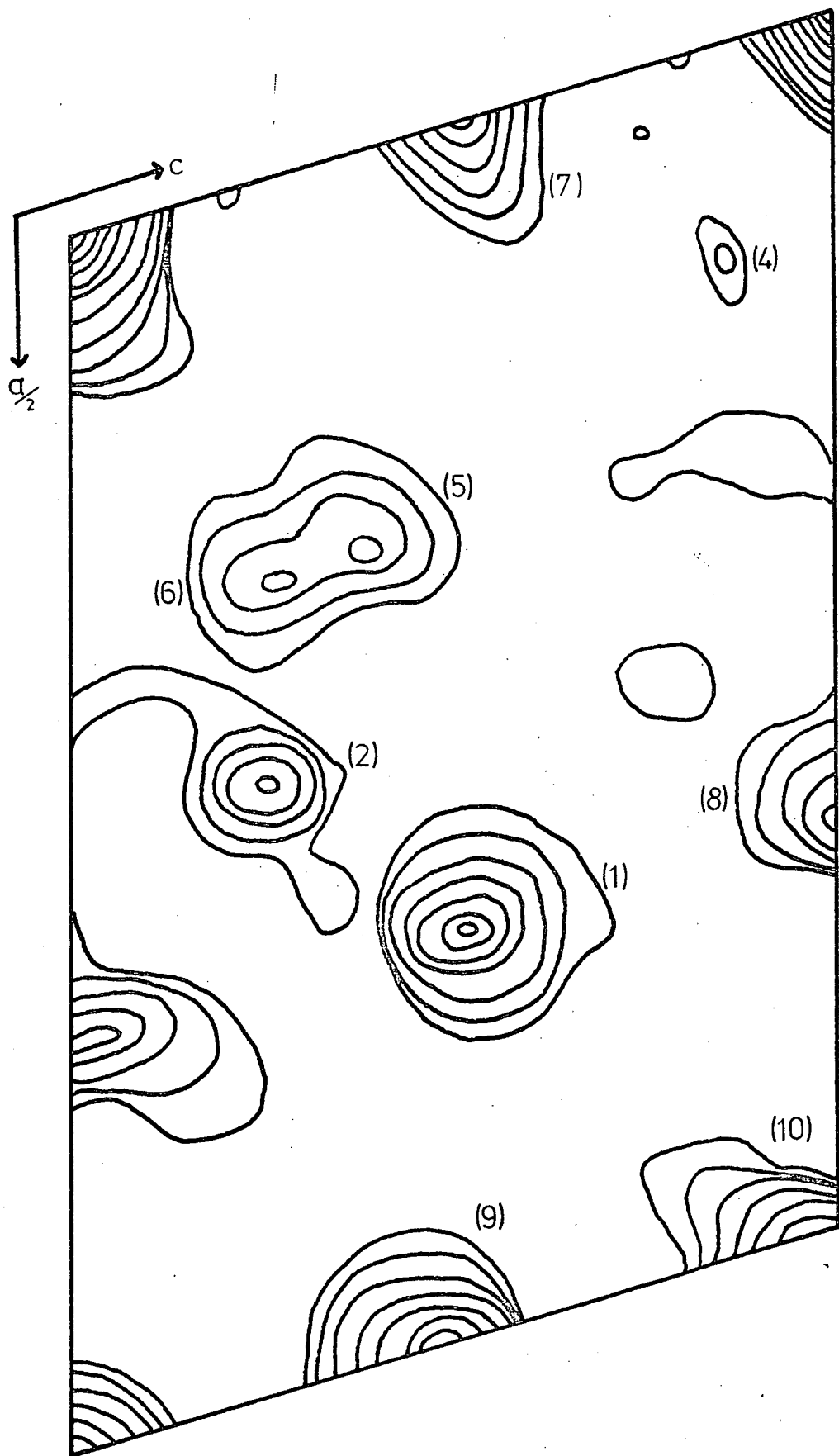


Fig. 4.1 Patterson section $y=0$
 $\text{Cs}_2\text{VCl}_5 \cdot 4\text{H}_2\text{O}$

cell at the special position of space group $C2/m$, $2(a)$ $(0,0,0)$ and $(1/2,1/2,0)$. For convenience the peaks of the Patterson map are labelled numerically in Fig. 4.1 and will be referred to as such. As a starting point the largest non-origin peak (1), of height 268 relative to the origin peak of height 856, was treated as a Cs-Cs vector. The second largest peak (2), of height 196 was assigned as resulting from a V-Cs interatomic vector. Since the vanadium had already been fixed at the origin, then peak (2) becomes a possible Cs location in the real cell at a position $4(i)$, with coordinates of approximately $(0.31,0,0.24)$.

In seeking possible Cl locations in the real cell a possibility exists that there is at least one chlorine coordinated to the vanadium atom. On the basis of the sum of reported⁷² ionic radii of V^{3+} (0.625 \AA) and Cl^{-} (1.81 \AA) such a bonded chlorine would be expected to lie at less than 2.5 \AA from the origin. There is only one peak, (4), of height, 31, in the Patterson at about this distance (Fig. 4.1). This Cl location (4), with coordinates of approximately $(0.10,0,0.87)$ is supported by a possible Cs-Cl vector at (5). If location (4) represents a Cl ligand attached to the vanadium atom, then the symmetry operation of the space group fixes a related Cl in the trans- configuration on the opposite side of the origin. It is possible that the remaining chlorines may also be bonded to the vanadium, but this can be ruled out because there are no other vectors of sufficient weight close enough to the origin peak. The chlorines remaining were located from the reasonably large possible Cs-Cl vectors (6) of height 101, and (7) of height 114, giving two locations for such chlorines at $2(d)$ $(0,1/2,1/2)$ and $4(i)$ $(0.30,0,0.75)$.

This allocation of vectors gave a model containing all Cs, V and Cl atoms. This model was used to calculate structure factors corresponding to the 243 observed reflections. After initial interlaying scaling had been carried out, a residual factor of 26% was obtained from a comparison of observed and calculated structure factors. The signs of the calculated

structure factors were then allocated to the observed data, and Fourier and difference Fourier syntheses were calculated. The atomic positions appeared as peaks in the Fourier map with peak heights consistent with their respective atomic numbers. There were no anomalous negative regions occurring at these positions in the difference Fourier.

The assignment of the remaining oxygens of the water molecules was made on the basis of a peak occurring at approximately (0.06,0.2,0.2) in the Fourier and difference Fourier maps. Inspection of the relevant Patterson map section with $y = 8/40$ showed a possible Cs-OH_2 vector consistent with the allocation of the oxygens.

The completed model was used to calculate further structure factors, and the structure was refined by the full-matrix least-squares method initially on the atomic coordinates. The R factor, as defined in Section 1.2, at this stage was 18%. Suitable trial values of isotropic temperature factors were introduced, these being obtained by analogy with values for similar atoms in structures discussed in Chapter 3. The refinement continued down to a residual factor of 13%. Inspection of the relationship between individual observed versus calculated structure factors revealed several reflections which showed poor correlation. The intensity of these particular reflections were checked. It was found that all were either in the wide angle range and showed α, β splitting or occurred along streaks on the film making them difficult to measure. Three reflections with very low intensity were deleted and several other more intense spots were measured on both sides of the film and the average value substituted in the calculations. Further cycles of least-squares refinement brought the residual factor down to 10.3%. However, in checking this refinement stage by Fourier and difference Fourier calculations it was noted that the eight-fold oxygen ligand position gave rise to a much smaller peak than was expected on the Fourier, and a slight "hole" or negative region on the difference Fourier map. This suggested that the ligand should be shifted to a point along the

y direction further away from the vanadium atom. A bond length calculation on the model with residual factor of 10.3% gave the V-OH_2 bond as 1.85 \AA , a value considerably shorter than an expected bond length of about 2.0 \AA found in the other compounds containing $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ ions discussed in later portions of this thesis. (Chapters 5 and 6).

Also the isotropic temperature factor of the water (5.88 \AA^2) was considerably greater than expected for such a ligand. As discussed earlier most of the contents of unit cell are concentrated in the plane (xOz) with the water molecules being the only groups outside this plane. Thus all the refinement along the \underline{b} direction is concentrated on the y coordinate of the oxygen atom. It must be remembered also that only four levels of data were collected along the \underline{b} -axis, thus the refinement was throwing all the errors onto two variables of the smallest atoms present. In the light of V-OH_2 bond lengths found in all other studies, it was decided to carry out the selection and refinement of the water position by difference Fourier methods. Beginning again with the partial Cs_2VCl_5 model included in a structure factor calculation but with the oxygens excluded, least-squares refinement gave a residual factor of 13%. From this a difference Fourier was calculated with sections of $1/100 \underline{b}$. The relevant section with the missing oxygen peak occurred at $21/100 \underline{b}$ and this was contoured on the plotter and the centre of the peak found by measurement to have fractional coordinates of (0.0057, 0.209, 0.206). Inclusion of this fixed position for the oxygen atom and refinement of overall structure resulted in a residual factor of 10.6% and gave a V-OH_2 bond length of 1.983 \AA . This is in good agreement with the average V-OH_2 bond length of 2.01 \AA found in the other related compounds reported herein. A final Fourier showed good peak height correlation and the difference Fourier showed no anomalies at the new oxygen position. At this stage the structure refinement was concluded. A comparison of observed and calculated structure factors is given in Appendix 3 as Table A.3.10.

For reasons discussed in Section 1.5 anisotropic temperature factors were not included in the refinement cycles. Together with the four layer-scale factors the maximum number of variables refined in the least-squares method was 19. The 243 observed reflections therefore provided more than ten data items per variable, and this was considered sufficient for structure refinement.

Data showing atomic coordinates and isotropic temperature factors, and some bond lengths and angles are shown as Tables 4.4 and 4.5. The standard deviations attached to these data refer to the deviations calculated from the least-squares and bond lengths computer programs (Appendix 1), and do not take into account errors inherent in intensity measurement or in the measurement of unit cell dimensions.

It can be seen from Table 4.4 that the final temperature factors calculated for the heavier atoms have relatively low values. This probably arises in the refinement stages to compensate for errors occurring in intensity data because of the neglecting of absorption corrections. (See also Section 1.5.1).

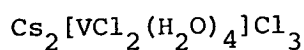
4.2.3. Description of the Structure

The structure of $\text{Cs}_2\text{VCl}_5 \cdot 4\text{H}_2\text{O}$ is shown viewed along [010] in Fig. 4.2. The Fourier section with $y = 0$ is also shown. (Fig. 4.3). The vanadium atoms are located at the two-fold special position (0,0,0) and (1/2,1/2,0). Each vanadium is at the centre of a complex $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ ion, the chlorines of which are trans to one another with $\text{V-Cl} = 2.361 \text{ \AA}$, and occupy a four-fold (x,0,z) position such that the line Cl-V-Cl lies in the planes with $y = 0$ and $y = \frac{1}{2}$. The oxygen ligands with $\text{V-OH}_2 = 1.983 \text{ \AA}$ are in an eight-fold (x,y,z) general position, four such ligands thus forming a rectangular plane with the vanadium at the centre.

The complex ion is distorted from D_{4h} tetragonal symmetry, the bond angles being 91.10° for Cl-V-OH₂, 92.0° for H₂O-V-OH₂. The H₂O-OH₂

TABLE 4.4

Atomic Coordinates and Isotropic Temperature factors



(Standard deviations in parenthesis)

Atom	Position	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$	$B(\sigma_B)$
V	2(a)	0	0	0	.98(7)
Cs	4(i)	0.2980(1)	0	0.2442(1)	.71(2)
Cl(1)	4(i)	0.1098(2)	0	-0.1273(5)	1.35(7)
Cl(2)	4(i)	0.3072(2)	0	0.7518(6)	1.76(7)
Cl(3)	2(d)	0	0.5	0.5	1.86(10)
O(H ₂ O)	8(j)	0.0557	0.209	0.206	2.99(20)

TABLE 4.5

Distances and Angles

(Standard deviations in parenthesis)

Complex ion	
V-Cl(1) = 2.361(2) Å	Cl(1) - OH ₂ = 3.054(8) Å and 3.113(1) Å
V-OH ₂ = 1.983(10) Å	
< Cl(1)-V-OH ₂ = 91.1(1)°	
< H ₂ O-V-OH ₂ = 92.0(2)°	
Other closest approach distances	
Cs-Cl(1) = 3.612(1) and 3.696(1) Å	
Cs-Cl(2) = 3.520(3) and 3.615(1) Å	
Cs-Cl(3) = 3.528(1) Å	
Cl(2)-OH ₂ = 2.973(7) Å	
Cl(3)-OH ₂ = 3.102(5) Å	

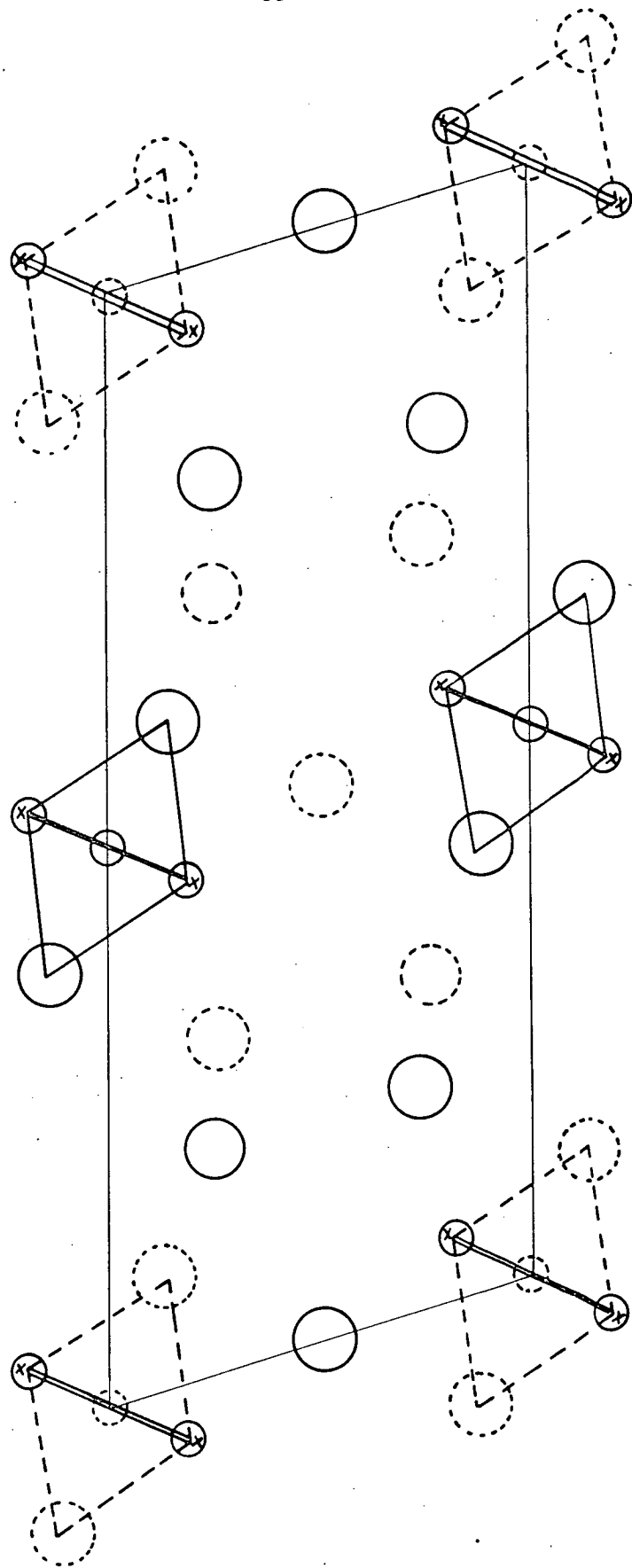
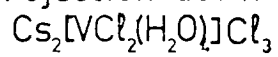


Fig. 4.2 Projection down [010]



---- in plane $y=0$



— in plane $y=\frac{1}{2}$



(x) = H_2O

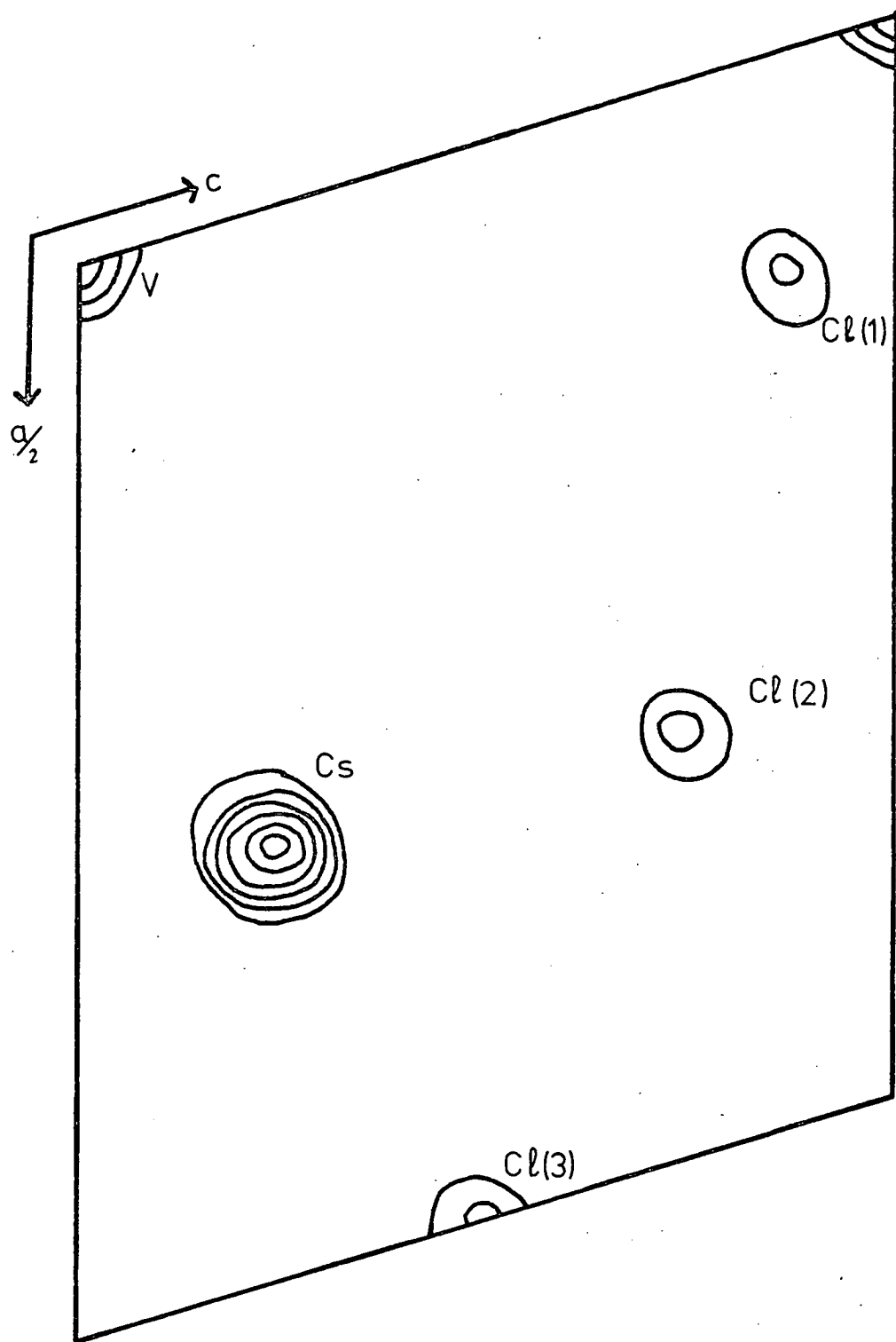


Fig. 4.3

FOURIER SECTION $y=0$ $Cs_2[VC l_2(H_2O)_4] Cl_3$

distance in the octahedra is 2.585 \AA .

Of the remaining non-bonded chloride ions those labelled Cl(3), occupy equivalent positions $(0,1/2,1/2)$ and $(1/2,0,1/2)$ and the other four Cl(2), are located in a four-fold $(x,0,z)$ location. The caesium ions are likewise in $4(i)$, $(x,0,z)$ positions.

Each caesium ion is surrounded by eight chlorines as nearest neighbours (Fig. 4.4); four of these are Cl(2) ions from two planes separated by $b/2$, one is a Cl(3) ion from the (010) plane and the remaining three are Cl(1) ligands from two different octahedra. This arrangement is close to the CsCl body-centered cubic structure.

The nearest neighbours of the chloride ions Cl(2), form a distorted octahedron comprising four caesium ions with $\text{Cs-Cl} = 3.520 \text{ \AA}$ and two water ligands from different complex ions with $\text{Cl-OH}_2 = 2.973 \text{ \AA}$ (Fig. 4.5).

The other type of chloride ion Cl(3) is also surrounded by six nearest neighbours occupying the corners of a slightly distorted octahedron. Two of these are caesium ions in the same plane with $\text{Cs-Cl} = 3.528 \text{ \AA}$; the others are water ligands from four different complex ions with $\text{Cl-OH}_2 = 3.102 \text{ \AA}$ (Fig. 4.6). Each chlorine ligand Cl(1) has three caesium ions at 3.696 \AA as nearest neighbours.

The overall structure is thus one of close packing of Cs^+ , $[\text{VCl}_2(\text{H}_2\text{O})_4]^{+}$ and Cl^- ions in layers with $y = 0$ and $y = 1/2$ perpendicular to the b axis. The major forces holding these species and layers together is therefore most probably electrostatic attraction. The distance of closest approach of the chloride ions Cl(2) and Cl(3) to the water ligands is less than 3.2 \AA . Since the sum of reported⁷² ionic radii of Cl^- and O^{2-} is 3.21 \AA , it is likely that there is some hydrogen bonding between the chloride ions of one layer and coordinated water molecules of octahedra centered in planes on either side of this layer. The absence of waters of crystallization in this compound precludes the presence of H-bonded "cages" of water molecules linking octa-

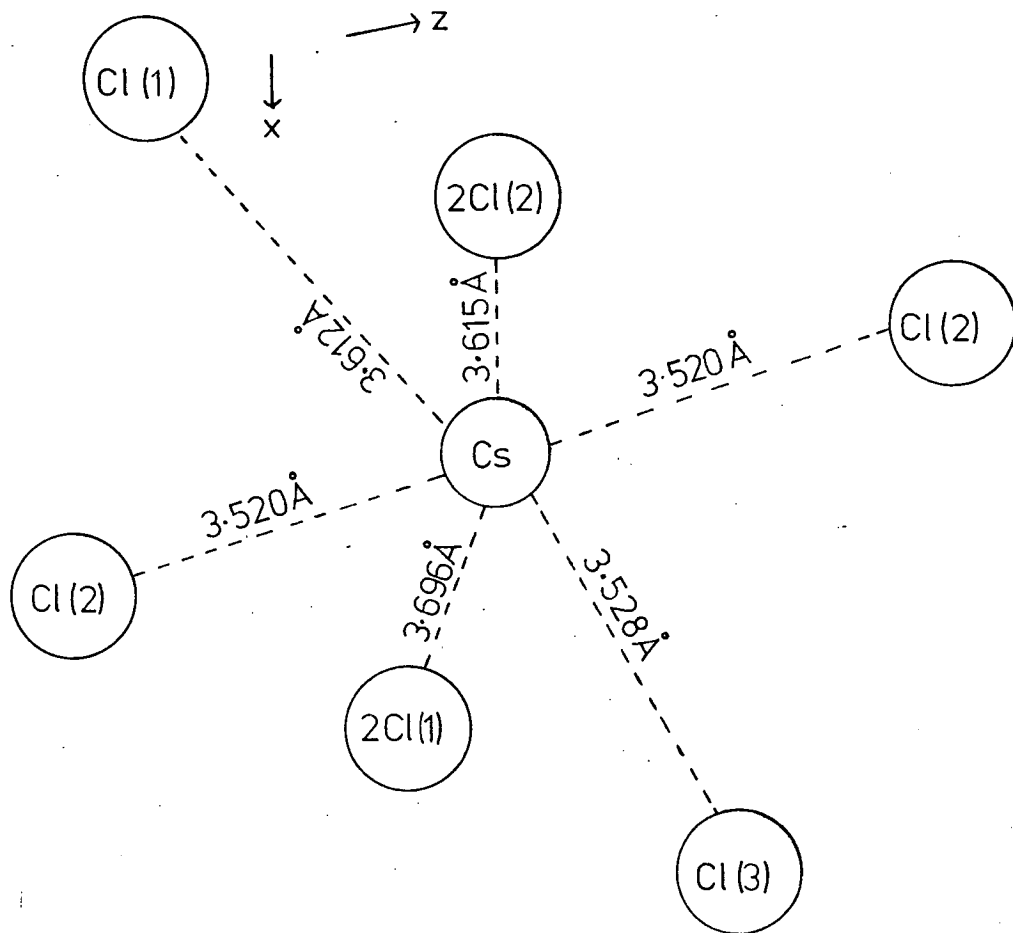
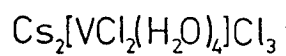


Fig. 4.4 Projection on [010]

Showing eight fold coordination of chlorines about the caesium ions.



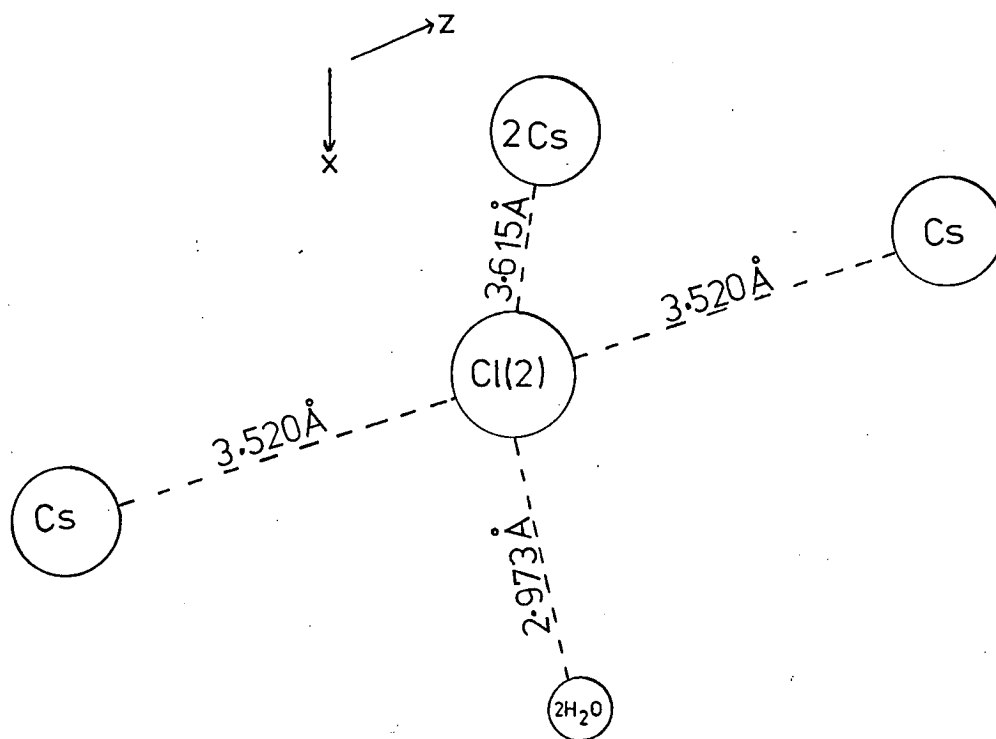


Fig. 4.5

Projection down $[010]$
 Showing distorted octahedral environment of
 $\text{Cl}(2)$ ions. $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$

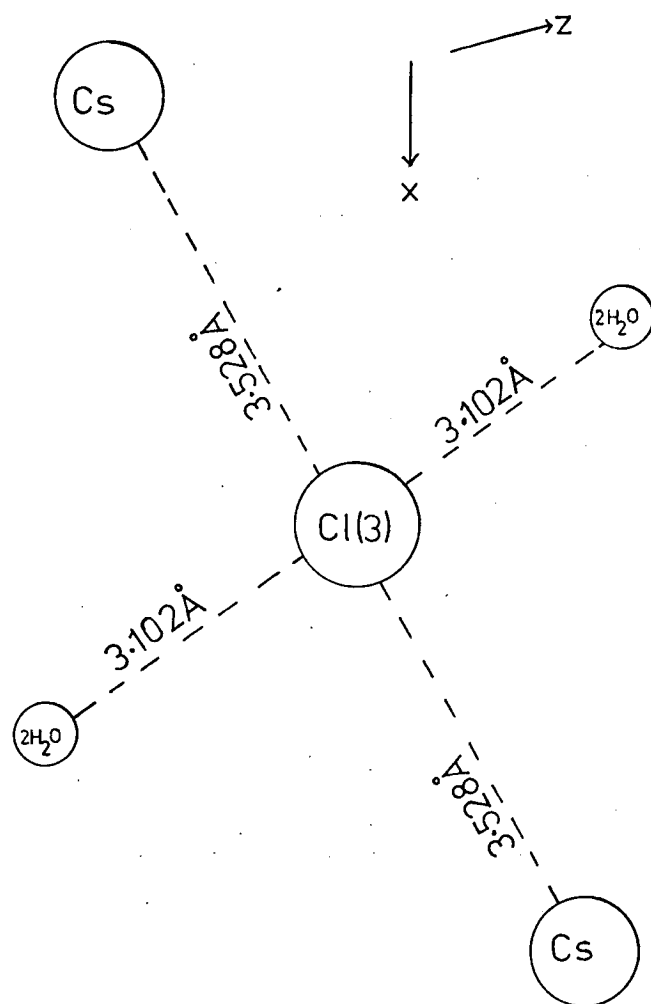
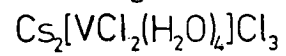


Fig. 4-6

Projection down [010]

Showing octahedral environment of Cl(3) ion.



hedra in chains, as has been described in $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}\cdot 2\text{H}_2\text{O}$ ^{84,85} and suggested for $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl}\cdot 2\text{H}_2\text{O}$ ⁸³.

The correct formula of this compound is thus $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$, and it should be named as dicaesium trans-dichlorotetraquovanadium (III) trichloride.

4.3. The Structure of $\text{Cs}_2\text{VBr}_5\cdot 4\text{H}_2\text{O}$

The work on this structure was jointly undertaken by Podmore⁶¹ and the author. The author collaborated to the extent of supervising and advising on the X-ray data collection process, and assisting in carrying out the computational work involved in the structure determination. The details of this structure determination have been presented in Podmore's Ph.D. Thesis⁶¹.

The unit cell dimensions were initially obtained from oscillation and zero-level equi-inclination Weissenberg X-ray photographs, and refined on powder data (See above, Table 4.2) obtained from a Philips powder diffractometer using Cu K_α radiation and KCl as an internal calibrant. These dimensions and other crystallographic data are shown above in Table 4.3 by comparison with data from $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$.

A single crystal of approximate dimensions 0.5 x 0.2 x 0.2 mm was mounted in a capillary using the technique described for $\text{Cs}_2\text{VCl}_5\cdot 4\text{H}_2\text{O}$. (Section 4.2). Single crystal X-ray data were collected by the equi-inclination Weissenberg method on 4-film packs. These data were taken about the monoclinic b-axis for the five levels hnl ($n = 0-4$), giving a total of 511 observed reflections. The data were corrected for Lorentz and polarisation factors but not for absorption.

Inspection of the X-ray powder data and single-crystal photographs suggested that this compound was isomorphous with that reported here for $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$, and hence the structure refinement was carried out using a model for $\text{Cs}_2\text{VBr}_5\cdot 4\text{H}_2\text{O}$ derived by analogy from the chlorine compound. The structure was refined by varying atomic coordinates and isotropic

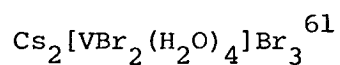
temperature factors using the technique of full-matrix least-squares refinement. The lowest residual factor obtained was 17%. The structure could be refined by correcting for absorption as the crystal used was a relatively large one. However, Fourier and difference Fourier maps of the structure with this residual factor showed no anomalies, so the refinement was terminated at this point.

Relevant data showing atomic coordinates, isotropic temperature factors and bond lengths and angles are shown in Tables 4.6 and 4.7. The standard deviations attached to the coordinates were calculated from the least-squares refinement program and do not take into account errors in data collection or unit cell measurements. A comparison of observed and calculated structure factors is shown in Appendix 3 as Table A3.11. This compound is isomorphous with $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$ and hence should be formulated as $\text{Cs}_2[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br}_3$, dicaesium trans-dibromotetraquovanadium (III) tetrabromide.

The data obtained from this structure determination can be correlated with the other V(III) structures reported in this work and this will be amplified in Chapter 7.

TABLE 4.6

Atomic coordinates and isotropic temperature factors

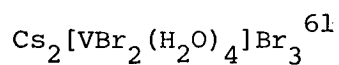


(Standard deviations in parenthesis)

Atom	Position	x (σ_x)	y (σ_y)	z (σ_z)	B (σ_B)
V	2(a)	0	0	0	1.01(5)
Cs	4(i)	0.2982(1)	0	0.2452(1)	1.19(2)
Br(1)	4(i)	0.1111(1)	0	-0.1325(2)	1.55(3)
Br(2)	4(i)	0.3070(1)	0	0.7473(2)	1.73(3)
Br(3)	2(d)	0.5	0	0.5	1.57(3)
O(H ₂ O)	8(j)	0.5060(4)	0.2271(18)	0.1930(11)	1.55(19)

TABLE 4.7

Bond lengths and angles



(Standard deviations in parenthesis)

V-Br(1)	2.497(1)	< Br(1)-V-OH ₂	90.3(2)
V-OH ₂	2.060(7)		
Cs-Br(1)	3.775(1)		
Cs-Br(2)	3.607(2)		
Cs-Br(3)	3.677(1)		
Br(1)-Br(2)	3.954(1)		
Br(1)-OH ₂	3.229(6)		
Br(2)-OH ₂	3.091(5)		
Br(3)-OH ₂	3.175(6)		

Chapter 5

Crystal Structures of Vanadium(III) Aqua Chloro Complexes

II. RbVCl₄.6H₂O

5.1. Introduction

The rubidium salt, RbVCl₄.6H₂O contains the same number of atoms as Cs₂VCl₅.4H₂O (Chapter 4) but has a different overall stoichiometry. It is of interest to see if this rubidium salt also contains the [VCl₂(H₂O)₄]⁺ complex ion as found in the caesium salt. Further interest centres around overall packing considerations, the possible presence of hydrogen bonding and the relationship of this compound to the other V(III) complexes discussed in this thesis.

5.2. Experimental

The green crystalline material was prepared by Podmore⁶¹ by passing hydrogen chloride into a solution of vanadium(III) chloride and rubidium chloride. Similar problems were encountered in mounting single crystals as for Cs₂[VCl₂(H₂O)₄]Cl₃ (Section 4.2), and a single crystal was isolated in the same way. This needle-shaped crystal of approximate dimensions 0.2 x 0.1 x 0.1 mm was used for intensity data collection.

Preliminary lattice parameters were obtained from oscillation and equi-inclination Weissenberg photographs, and refined by least-squares methods on powder data (Table 5.1) collected from a Philips powder diffractometer using Cu K_α radiation, and KCl as an internal calibrant. Unit cell parameters are shown in Table 5.2.

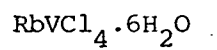
Collection of intensity data from the single crystal of this compound was carried out using the equi-inclination Weissenberg technique, described in Section 1.3.3. Trial photographs having shown the diffraction spots to be of a regular shape, the non-integrated data collection technique was

TABLE 5.1
X-Ray Powder Data⁶¹

RbVCl ₄ ·6H ₂ O		
$\sin^2 \theta_{\text{obs.}}$	$\sin^2 \theta_{\text{calc.}}$	Index
80.3 vs	80.5	1 1 0
98.5 w	97.9	0 2 0
165.9 m	166.2	1 1 1
322.8 vs	322.0	2 2 0
345.0 s	342.9	0 0 2
361.4 w	362.1	1 3 1
390.7 s	391.8	0 4 0
425.2 w	423.4	1 1 2
438.7 w	440.8	0 2 2
564.9 w	567.0	2 0 2
616.4 m	615.9	2 4 0
666.4 m	664.9	2 2 2
697.6 w	701.6	2 4 1
727.4 m	724.5	3 3 0
755.1 w	753.9	1 5 1
809.0 vw	810.3	3 3 1
874.4 m	871.6	3 1 2
995.8 vw	994.3	4 2 0
1011.9 w	1011.1	1 5 2
1104.9 w	1105.6	2 6 0
1217.9 w	1224.4	0 6 2
1259.5 s	1255.9	1 7 0
1290.1 w	1288.1	4 4 0
1349.3 vw	1341.6	1 7 1
1446.0 vw	1448.5	2 6 2
1509.2 w	1510.7	5 1 1
1569.0 s	1567.2	0 8 0
1694.7 vw	1693.6	2 2 4

TABLE 5.2

Crystallographic Data



a	$10.291 \pm 0.005 \text{ \AA}$
b	$15.566 \pm 0.007 \text{ \AA}$
c	$8.319 \pm 0.005 \text{ \AA}$
z	4
d _{obs}	1.93 g/cc^{95}
d _{calc}	1.93 g/cc
Systematic Absences	$\underline{hkl}: \underline{h+k} = 2n+1$ $0\underline{k}\underline{l}: \underline{l} = 2n+1$ $\underline{h}0\underline{l}: \underline{l} = 2n+1$
Space Group	Orthorhombic Cccm

was employed rather than the more time consuming integrating method. This time-saving was required because of the extreme instability of the compound.

These preliminary data had also shown the compound to be orthorhombic, and intensity data were collected down the c-axis for levels hkn ($n = 0-4$), giving a total of 161 observed reflections. More reflections could have been recorded over longer exposure times or about the other two orthorhombic axes. This was, in fact, tried during the course of data collection but the crystals decomposed during the period of trial data collection. The data that were collected came from a crystal whose hk5 level showed extreme distortion of spots and obvious signs of crystal decomposition, and hence could not be used for further data collection about other axes.

The observed intensities of reflections were estimated visually against a standard scale and corrected for Lorentz and polarisation effects. Because of the small size of the crystal used, corrections were not made for absorption. (See discussion Section 1.5.1).

Inspection of the Weissenberg photographs taken about the c-axis, and from zero-level (short-term exposure) photographs taken about the other two axes, revealed the compound to be orthorhombic, and showed that reflections were systematically absent for hkl: $h+k = 2n+1$, Ok \bar{l} : $\bar{l} = 2n+1$ and hOl: $\bar{l} = 2n+1$. The axes chosen corresponds to the standard orientation used in the International Tables of Crystallography⁹, and the absence pattern corresponds to the space groups Cccm or Ccc2. The subsequent structure determination confirmed the choice of the centrosymmetric space group Cccm used for the calculations. Using the reported density of 1.93 g/cc^{95} , and the volume of the unit cell, it was calculated that there were four formula units of $\text{RbVCl}_4 \cdot 6\text{H}_2\text{O}$ per unit cell.

5.3. Structure Determination and Refinement

The crystal has the space group Cccm but the Patterson function can be calculated in the Patterson Group, Cmmm, of higher symmetry. (Section 1.2.2). A three dimensional Patterson function was therefore calculated in this space group Cmmm, the required sections being taken along the c -axis at intervals of $1/40$ for levels 0-20. The symmetry elements of the crystal space group Cccm manifest themselves as vector concentrations in the relevant Harker planes (Oyz), (xOz) and (xyO), and in the Harker lines ($xO\frac{1}{2}$), ($Oy\frac{1}{2}$) and (OOz). Several attempts were made to interpret this Patterson function using the information contained in these Harker lines and planes. The interpretation was complicated by the appearance of many possible vector peaks on the various sections. The description that follows is of a solution of the Patterson function which provided a partial model for the molecule, and which led to satisfactory structure completion and refinement. The allocation of the main interatomic vectors in the Harker plane (xyO) and in the plane with $y = \frac{1}{4}$ of the Patterson function is shown in Figs. 5.1 and 5.2.

The relatively heavy atom in this structure is the Rb^+ ion, and this must occur in one of the four-fold special positions as must the central vanadium ion. Along the Harker line (OOz) the only peaks occur at $(0,0,0)$ and $(0,0,1/2)$, suggesting that the main scattering matter in the unit cell lies in the planes with $z = 0$ and $z = \frac{1}{4}$. If the Rb^+ ion is located at 4(a), $(0,0,1/4)$ then Rb-Rb vectors would be expected at $(0,0,1/2)$, $(1/2,1/2,0)$, and $(1/2,1/2,1/2)$. Large peaks of relative height 737, 960 and 548 respectively do occur at these positions. (Origin peak, 1260). It is possible then that the vanadium atoms can occur in either planes with $y = 0$ or $y = \frac{1}{4}$. Examination of the other four-fold special positions available eliminates all but 4(f) $(1/4,3/4,0)$ or 4(e) $(1/4,1/4,0)$ positions, on the grounds that suitable Rb-V and V-V vectors only show up on the Patterson for

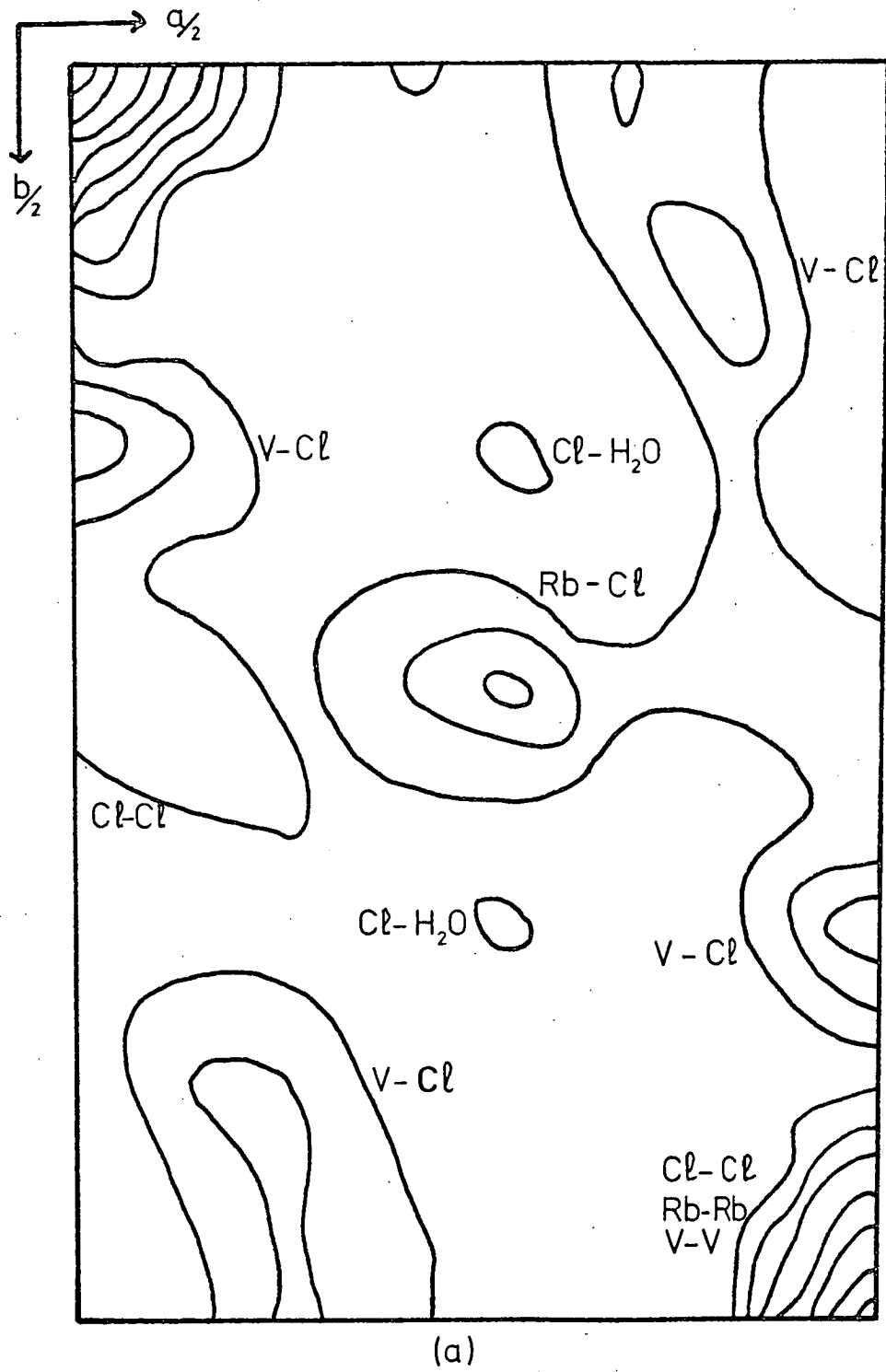


Fig. 5.1 Patterson section $z=0$
 $\text{RbVCl}_4 \cdot 6\text{H}_2\text{O}$

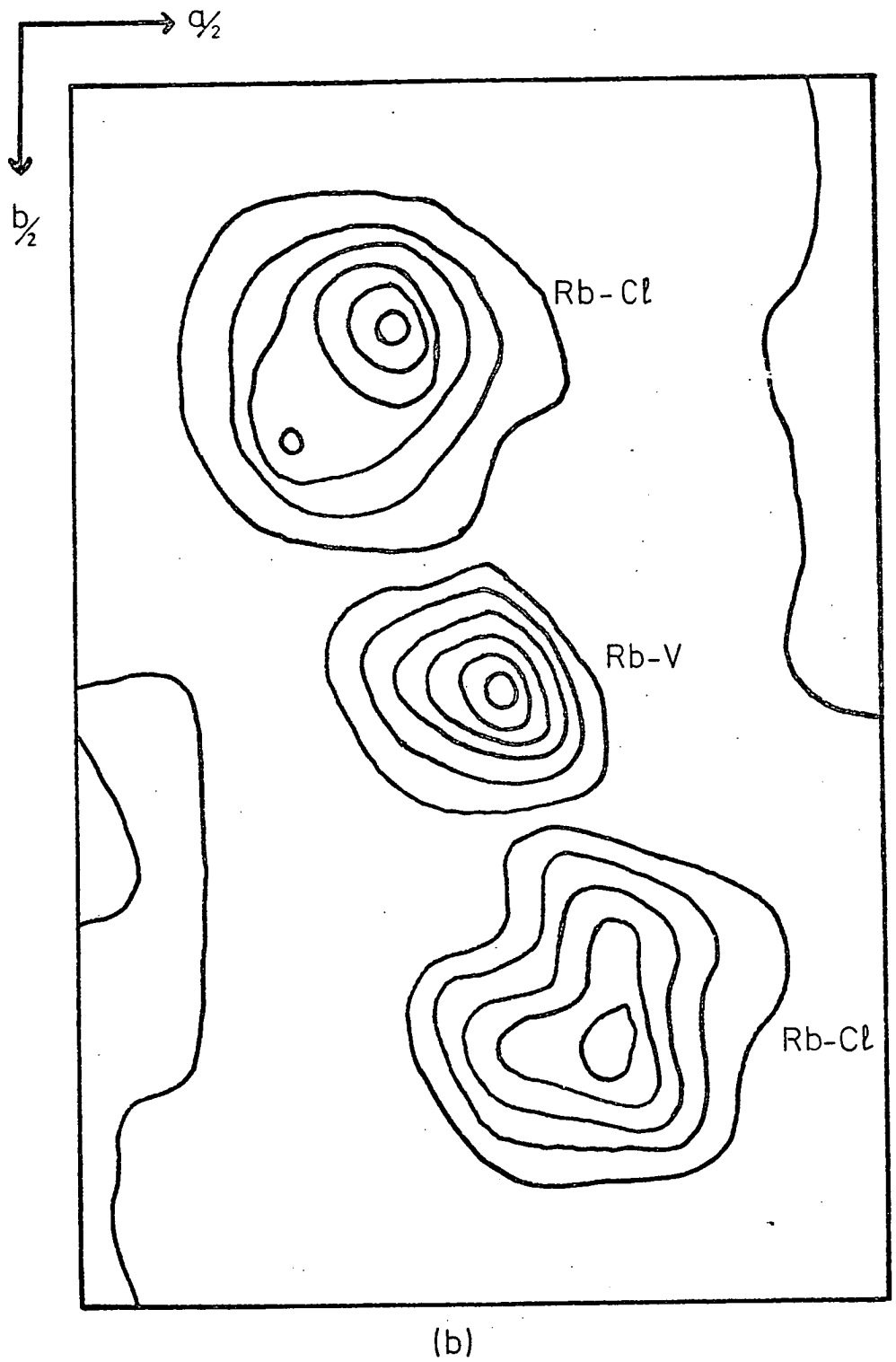


Fig.5.2 Patterson section $z=0.25\text{RbVCl}_4 \cdot 6\text{H}_2\text{O}$

these combinations with the Rb^+ position at 4(a). Since both available positions are at this stage equivalent, the vanadium was placed at 4(e) $(1/4, 1/4, 0)$.

In looking for possible chlorine positions it was thought best to search for V-Cl vectors of less than 2.5 \AA corresponding to expected bond lengths for this pair of atoms⁷². Inspection of the Patterson revealed only the one peak of height 130, close enough to the origin to be considered. (Fig. 5.1). Confirmation of this as a V-Cl vector comes from the relatively large peak of height 273, in the level with $z = 1/4$, corresponding to an Rb-Cl vector (Fig. 5.2). Thus the chlorine ligands were placed at a position of type 8(l), $(x, y, 0)$ locating them in a trans- configuration with respect to the vanadium metal ion. This allocation of interatomic vectors gave a possible model for the structure containing the Rb, V and 4 Cl atoms.

With this partial model of the structure it became possible to proceed with the identification of the complete structural unit. Structure factors were calculated corresponding to all the observed reflections, and the signs of these used to produce a Fourier and difference Fourier with sections of 0/40 to 10/40 along the c axis. From peaks on the $(xy0)$ plane a further eight-fold position could be assigned to the remaining packing chlorines, and a possible sixteen-fold position for the oxygens of the bonded water ligands. This latter position agreed with the type of octahedral orientation found in other similar molecules (Chapters 4 and 6). Upon further structure factor calculations, however, it was found that the residual factor increased from 37% to 43%. While the consequent Fourier showed a reasonable peak for the chlorine added, that which represented the proposed oxygen position was only about half the expected height.

On the difference Fourier map, however, a relatively large hole appeared where the oxygen of the water molecule was presumed to be. Deletion of this oxygen position and retention of the chlorine led to an R-factor calculation of 28% which suggested a more reasonable structural model.

Again, a Fourier and difference Fourier were calculated and the results examined for extra peaks. The only peaks on the difference Fourier suggestive of oxygen bonded ligands, were with the octahedral unit pointing along the z direction. Accordingly these were placed in an 8(i) (0,0,z) position, and the remaining bonded oxygens in 8(l) (x,y,0). Structure factors calculations resulted in a drop of the residual factor to 20%. The final task was to locate the remaining eight oxygen atoms.

Peaks on the difference Fourier suggested few possible locations for these atoms. Various positions of the type 8(h) (x,0,1/4) were tried, each time resulting in an approximate 10% rise in R-factor and the production of large holes in the resulting difference Fouriers. The four-fold positions cannot be occupied because they are too close to positions already filled by other atoms.

At this point it was thought that perhaps there were no other water molecules present, but a repeat analysis on the sample from which the crystal was taken confirmed their presence. Because there were no suitable peaks on the difference Fourier for the oxygens of these water molecules, it was decided to carry out several cycles of least-squares refinement on the $\text{Rb}[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_2$ portion of the molecule already obtained. Refinement of first the coordinates, and then the coordinates and isotropic temperature factors reduced the residual factor to 11%. At this stage a further Fourier and difference Fourier were calculated and examined for peaks which could suggest locations for the remaining water molecules. This time a small peak occurred on the difference Fourier with approximate coordinates (0.06,0.57,0), and this position of type 8(l) (x,y,0) was allocated to the remaining oxygen atoms. Further full-matrix least-squares refinement was carried out varying atomic coordinates and isotropic temperature factors of all atoms and the residual factor dropped to 9.5%. At this stage the shifts in parameters were less than the standard deviations. Because of this and because final

Fourier and difference Fourier maps showed no anomalies the structure refinement was concluded. Anisotropic temperature factors were not introduced into the refinement, because the observed data (161 reflections) did not provide enough data to justify their use. (See Section 1.5.1).

Relevant data, showing atomic coordinates, isotropic temperature factors and bond lengths and angles are shown in Tables 5.3 and 5.4. The standard deviations shown for these were calculated from the particular operations of the computer programs used, and do not include allowance for errors in intensity data collection and measurement of unit cell dimensions.

A comparison of observed and calculated structure factors after the last refinement cycle is shown in Appendix 3 Table A.3.11.

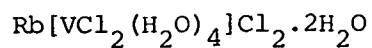
5.4. Description of the Structure:

The structure of $\text{RbVCl}_4 \cdot 6\text{H}_2\text{O}$ is illustrated in projection from $z = 0$ to $z = \frac{1}{4}$ along $[001]$ in Fig. 5.3. The vanadium atoms lie at centres of symmetry 4(e) $(1/4, 1/4, 0)$, $(1/4, 3/4, 1/2)$, $(3/4, 3/4, 0)$ and $(3/4, 1/4, 1/2)$, and are arranged in layers parallel to the (001) plane separated by $c/2 = 4.16 \text{ \AA}$. The complex $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ ions are oriented with a $\text{H}_2\text{O}-\text{V}-\text{OH}_2$ axis lying parallel to the c -axis, and the other two waters and the two trans-chlorine ligands occupy the corners of a slightly distorted rectangle around the V atom in the (001) plane. The oxygens of the water ligands occupy two different eight-fold positions, one of type 8(l), $(x, y, 0)$ with $\text{V}-\text{OH}_2 = 2.003 \text{ \AA}$ and the other of type 8(h), $(0, y, 1/2)$ with $\text{V}-\text{OH}_2 = 2.044 \text{ \AA}$. The chlorine ligands occupy equivalent eight-fold positions 8(l), $(x, y, 0)$, the V-Cl distance being 2.367 \AA . The bond angles within the octahedral complex ion are, within standard deviations, equal to 90° , the two $\text{H}_2\text{O}-\text{OH}_2$ distances are 2.862 and 2.65 \AA and the relevant Cl- OH_2 distances are 3.127 and 3.093 \AA . Thus there is only a very slight distortion from the tetragonal D_{4h} symmetry.

Each rubidium ion is surrounded by eight chlorines at the corners of a

TABLE 5.3

Fractional Atomic Coordinates and Isotropic Thermal Parameters



(Standard deviations in parenthesis)

Atom	Position	x (σ_x)	y (σ_y)	z (σ_z)	B (σ_B)
V	4(e)	0.25	0.25	0.0	1.96(8)
Rb	4(a)	0.0	0.0	0.25	1.69(5)
Cl(1)	8(l)	0.2115(3)	0.1001(2)	0.0	1.91(8)
Cl(2)	8(l)	0.8455(3)	0.1303(2)	0.0	1.44(8)
O(H ₂ O) ₁	8(k)	0.25	0.25	0.2457(18)	3.83(21)
O(H ₂ O) ₂	8(l)	0.4421(8)	0.2292(5)	0.0	3.72(25)
O(H ₂ O) ₃	8(l)	0.0510(7)	0.5748(5)	0.0	3.50(50)

TABLE 5.4

Distances and Angles

(Standard deviations in parenthesis)

Complex ion

$V-Cl(1) = 2.367(1) \text{ \AA}$	$H_2O(1)-OH_2(2) = 2.862(7)$
$V-OH_2(1) = 2.044(8) \text{ \AA}$	
$V-OH_2(2) = 2.003(4) \text{ \AA}$	
$Cl(1)-OH_2(1) = 3.127(6) \text{ \AA}$	
$Cl(1)-OH_2(2) = 3.109(3) \text{ \AA}$ and $3.093(3) \text{ \AA}$	
$\angle Cl(1)-V-OH_2(1) = 90.0(2)^\circ$	
$\angle Cl(1)-V-OH_2(2) = 90.3(1)^\circ$	
$\angle H_2O(1)-V-OH_2(2) = 90.0(3)^\circ$	

Other closest approach distances

$Rb-Cl(1) = 3.390(1) \text{ \AA}$
$Rb-Cl(2) = 3.312(1) \text{ \AA}$
$Cl(1)-OH_2(3) = 3.515(4) \text{ \AA}$
$Cl(1)-Cl(2) = 3.634(1) \text{ \AA}$
$H_2O(2)-OH_2(3) = 2.652(4) \text{ \AA}$
$Cl(2)-OH_2(2) = 3.092(3) \text{ \AA}$
$Cl(2)-OH_2(1) = 2.985(6) \text{ \AA}$
$Cl(2)-OH_2(3) = 3.152(4) \text{ \AA}$
$H_2O(3)-OH_2(3) = 2.554(4) \text{ \AA}$

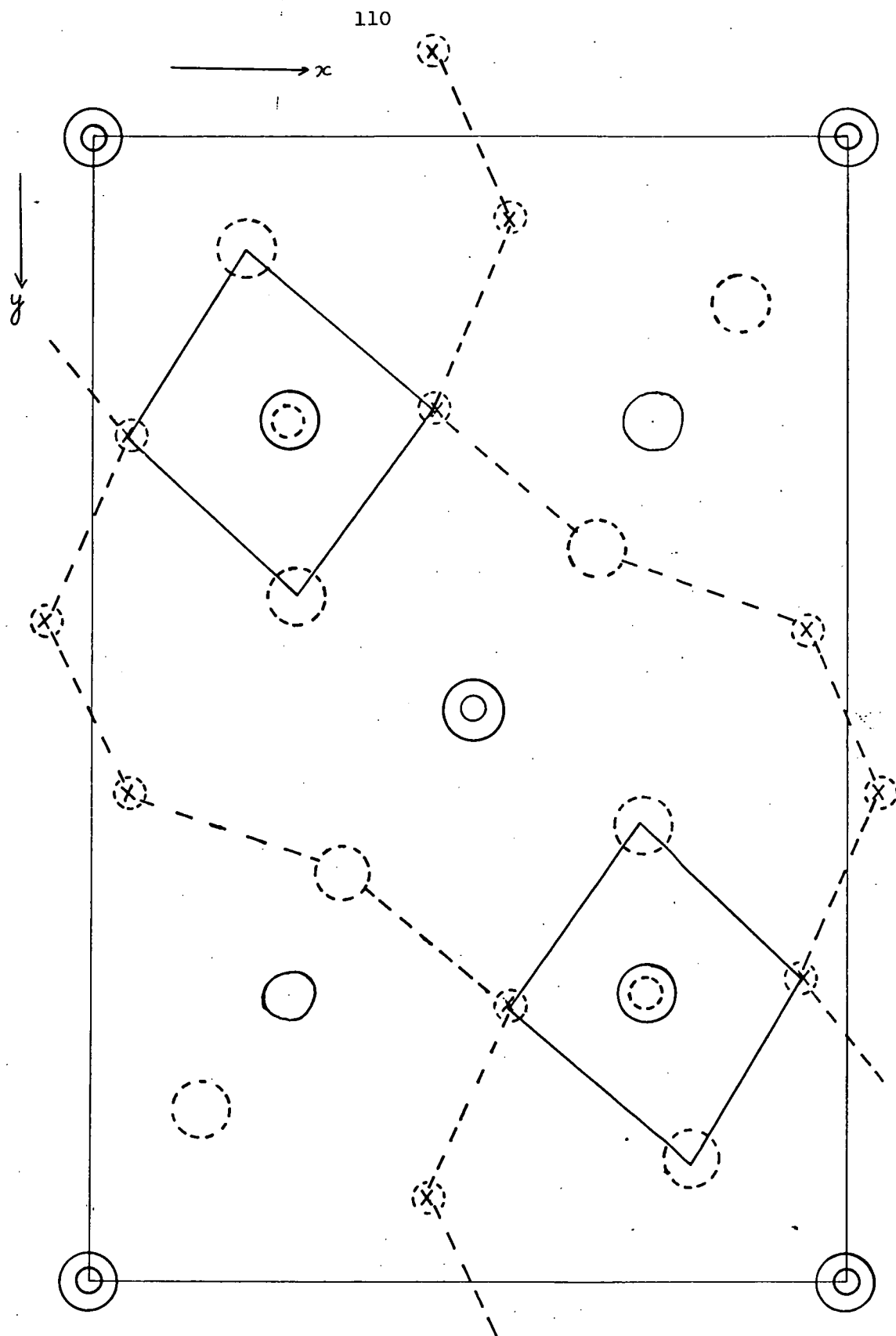
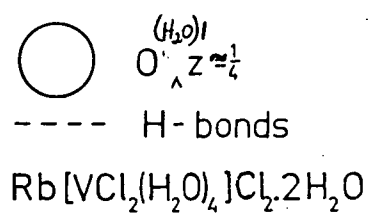
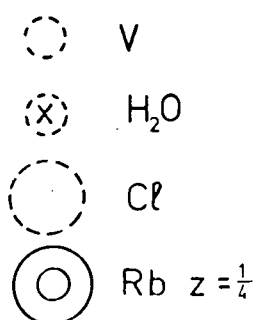


Fig. 5.3 Projection down $[001]$ from $z = 0$ to $z = \frac{1}{4}$



slightly distorted cube, similar to the CsCl structural type (Fig. 5.4). Four octahedra centred in two layers with $z = 0$ and $z = \frac{1}{2}$ each contribute one chlorine ligand, $\text{Rb-Cl} = 3.390 \text{ \AA}$, and two each of the remaining four chlorine are chloride ions in the planes with $z = 0$ and $z = \frac{1}{2}$ with $\text{Rb-Cl} = 3.312 \text{ \AA}$. The overall effect is to provide a series of "cages" in which the Rb^+ ions lie, holding the various sheets of octahedra together by strong electrostatic attraction.

Each chloride ion is surrounded by six nearest neighbours at the corners of a distorted octahedron (Fig. 5.5). Two of the neighbours are Rb^+ ions at 3.312 \AA , one a hydrate water molecule at 3.152 \AA and the other three are water ligands from different complex ions ($\text{Cl-OH}_2 = 2.985$ and 3.092 \AA). The complex ions can be regarded as being linked to form a sheet-like structure within alternate layers with $z = 0$ and $z = \frac{1}{2}$ perpendicular to the c -axis. In the layer with $z = 0$ each octahedral ion is linked to its neighbours in a chain along the $[110]$ direction via two hydrate water molecules, each of which may be a proton acceptor in two hydrogen bonds from ligand water molecules of two octahedra. The chloride ions in the same layer, lie along the $[1\bar{1}0]$ direction at points equidistant between chains of octahedra, and possibly accept one hydrogen-bond from a ligand water ($\text{Cl-H}_2\text{O} = 2.985 \text{ \AA}$), and a second from an hydrate water molecule ($\text{Cl-H}_2\text{O} = 3.152 \text{ \AA}$), which is in turn hydrogen-bonded to a water ligand of a complex ion in another chain ($\text{H}_2\text{O-H}_2\text{O} = 2.652 \text{ \AA}$), the whole forming a sheet-like arrangement in the (001) plane. There is also a possibility of weaker H-bonding between Cl^- ions in one layer and two water ligands of type 8(h) from complex ions in two different layers.

The sheets formed by hydrogen-bonding between chains of octahedra in planes with $z = 0$ and $z = \frac{1}{2}$ form a series of "cages" which are occupied by Rb^+ ions in planes with $z = \frac{1}{4}$ and $z = \frac{3}{4}$. Strong electrostatic bonding would, therefore, exist between these Rb^+ ions and the chloride ions in the sheets, ($\text{Rb-Cl} = 3.312 \text{ \AA}$) and there would also be electrostatic bonding

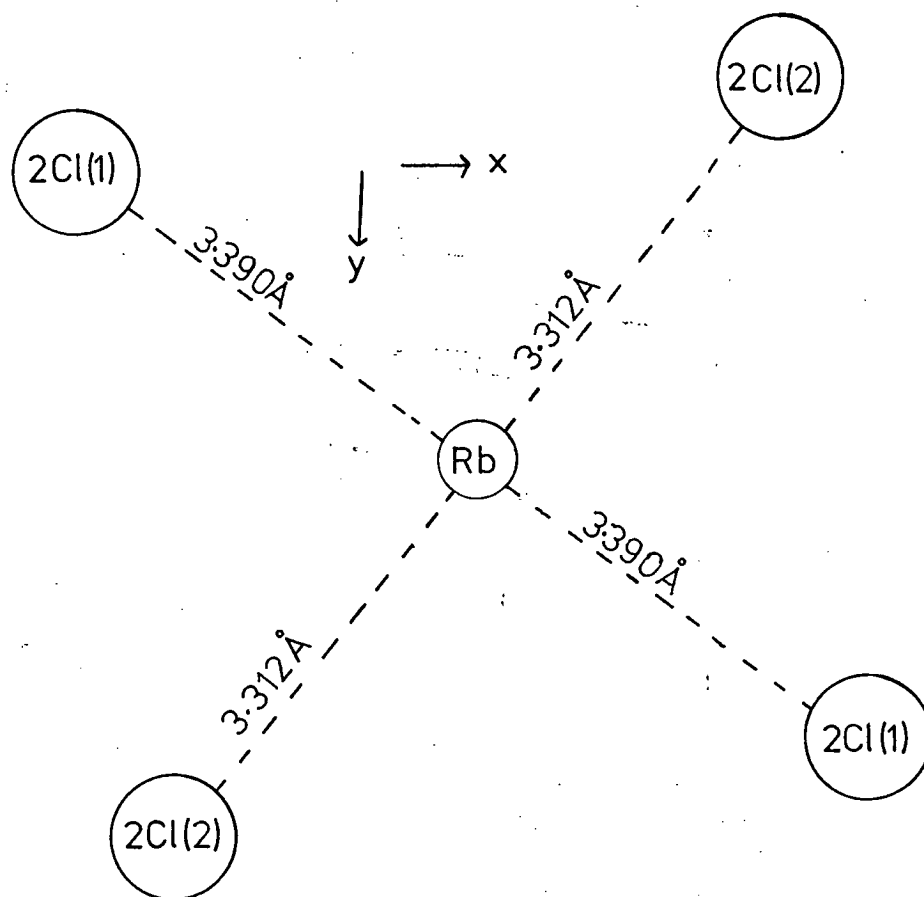
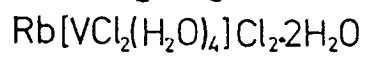


Fig. 5.4 Projection on [001]

Showing eight-fold coordination around Rb^+ .



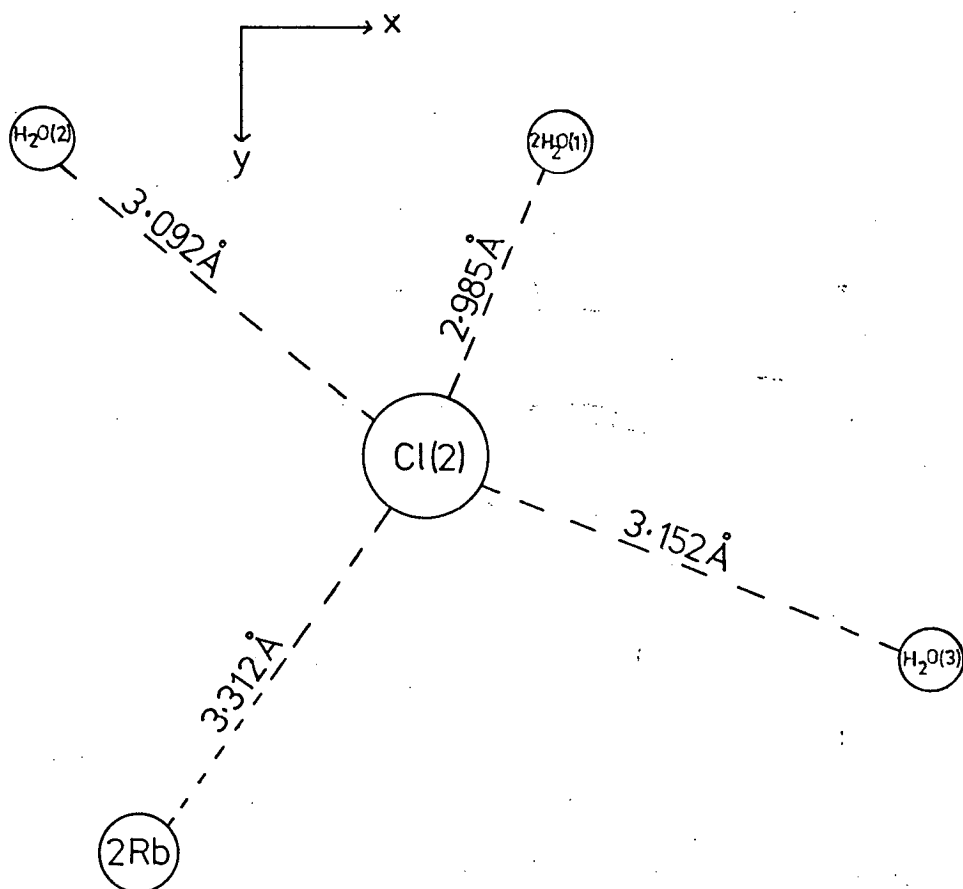


Fig. 5.5 Projection on [001] showing distorted octahedral environment of $\text{Cl}^-(2)$ ions.
 $\text{Rb}[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

between Cl^- ions and $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ ions. Thus the compound should be formulated as $\text{Rb}[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, rubidium dichlorotetraaquovanadium(III) dichloride dihydrate. Further discussion of this compound will be made in Chapter 7.

Chapter 6

Crystal Structures of Vanadium(III) Aqua Chloro Complexes

III. $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$ and $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$

6.1. Introduction

The crystal structures of $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$ and $\text{Rb}[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ discussed in Chapters 4 and 5 provide the first information on V(III)-Cl and V(III)-OH₂ bond distances in octahedral complex ions of vanadium. Some comparisons of these bond lengths with those in similar octahedra in, for example, $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ^{84,85} and $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ⁸³ could now be made. These comparisons are, however, restricted in scope by the different stoichiometry of the Rb and Cs salts of V(III) compared to those reported for Cr(III) and Fe(III), and by the different degrees of H-bonding in the structures.

In order to obtain direct structural comparisons a structure determination on $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ was commenced. Preliminary X-ray data collected on this compound suggested that it was monoclinic, space group $\text{P2}_1/\text{m}$, with cell dimensions of approximately $\underline{a} = 6.4$, $\underline{b} = 6.4$, $\underline{c} = 23.1 \text{ \AA}$, and $\beta = 99^\circ$ and with $\underline{z} = 4$. Refinement of this cell on X-ray powder data enabled all powder lines to be indexed. Three dimensional X-ray diffraction data were collected for $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ and a Patterson function calculated from these. Attempts to refine the structure on models derived from this Patterson map were unsuccessful, and there appeared to be no structural requirement for the long \underline{c} -axis. During attempts to solve the structure several other crystals were mounted, but each gave similar Weissenberg photographs. Because twinning is common to crystals of these V(III) compounds, it was suspected that this could be the cause of the problems for $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$. Accordingly attention was switched to the analogous bromo compound $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$.

6.2. Crystal Structure of $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$

6.2.1. Experimental

The sample used in this work was prepared by Podmore⁶¹ as a green crystalline compound, precipitated from vanadium(III) bromide solution by evaporation and cooling. The crystals were extremely unstable in air and moisture, and in most cases showed signs of twinning under microscopic examination. Even with the experience gained in mounting single crystals of other unstable compounds, it still required several attempts to finally select a small needle shaped crystal, coat it with nujol, and seal it in a soda-glass capillary tube. The crystal had approximate dimensions 0.2 x 0.1 x 0.1 mm.

The needle axis proved to be the monoclinic b-axis and subsequent equi-inclination Weissenberg photographs were taken with this b-axis as the axis of rotation. The preliminary determination of space group and cell dimensions were made using the Weissenberg technique with Cu K_α radiation. The cell dimensions were refined on X-ray powder data (Table 6.1), obtained from a Debye-Scherrer Camera using KCl as an internal calibrant⁶¹. These powder data are consistent with those reported by Nichols and Wilkinson⁹⁶. Crystallographic data ^{are} ~~is~~ listed in Table 6.2. This was the only compound handled in this study which proved too unstable for either Guinier-Hägg or Philips Diffractometer X-ray powder data collection. This extreme instability is characteristic of these vanadium(III) complexes and it was perhaps fortunate that a single crystal was mounted in this simple fashion under nujol; a technique that did not work for the slightly more stable compounds discussed in Chapters 4 and 5.

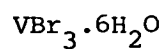
The monoclinic space group was uniquely determined to be $\text{P2}_1/\text{c}$, the absent reflections being for the conditions; $h0\ell$: $\ell = 2n+1$ and $0k0$: $k = 2n+1$. The allocation of unit cell edges was made according to the

TABLE 6.1
X-ray Powder Data⁶¹
 $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$

$\sin^2 \theta_{\text{obs.}}$	$\sin^2 \theta_{\text{calc.}}$	Index
176.4 m	177.8	0 1 1
266.6 w	272.2	1 0 -2
297.4 vs	296.8	0 1 -2
346.3 m	340.2	1 1 1
413.9 w	410.3	1 1 -2
549.9 vs	552.4	0 2 0
590.4 w	592.0	0 2 -1
644.1 vw	634.7	0 0 -4
687.6 m	690.2	1 1 3
725.0 m	722.8	2 1 0
804.8 m	808.6	2 0 2
839.0 w	846.1	1 0 4
884.8 s	889.8	1 2 2
1106.0 s	1104.5	1 2 3
1179.6 w	1177.6	2 1 3
1345.3 w	1349.8	2 0 4
1359.6 w	1360.9	2 2 2
1421.5 m	1428.0	0 0 -6
1490.7 m	1487.9	2 1 4
1597.4 m	1599.8	0 3 3
1656.6 m	1663.9	3 1 -3
1930.3 vw	1928.7	3 2 -2
2031.2 w	2028.8	1 2 -6
2114.3 w	2113.9	1 1 -7
2211.3 w	2209.5	0 4 0
2498.1 vw	2496.1	0 2 7
2563.4 vw	2566.5	0 4 -3
2755.3 m	2756.4	1 2 7
3309.2 w	3309.0	2 2 7
3525.6 w	3525.0	3 4 0

TABLE 6.2

Crystallographic Data



a	$6.408 \pm 0.004 \text{ \AA}$
b	$6.550 \pm 0.004 \text{ \AA}$
c	$12.300 \pm 0.007 \text{ \AA}$
β	$96.15 \pm 0.05^\circ$
d_{calc}	2.58 g/cc
d_{obs}	2.48 g/cc
z	2
Systematic Absences	$\underline{h0\ell}: \underline{\ell} = 2n+1$ $0\underline{k}0: \underline{k} = 2n+1$
Space Group	$P2_1/c$
Axis of Data Collection	\underline{b}
Observed Reflections	430 (372 used in refinement)

classification in the International Tables for X-ray Crystallography⁹ using the second monoclinic setting. The density of the compound was measured by the gradient tube method to be 2.48 g/cc. Taken in conjunction with the cell volume there are therefore two molecules of $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$ per unit cell.

A total of 430 non-integrated intensity data for hnl ($n = 0-4$), were recorded photographically by the Weissenberg equi-inclination technique using Cu K_α radiation and 4-film packs. The main reason for favouring non-integrated data collection was because it was suspected that the crystal would decompose before sufficient integrated data could be obtained. Intensities were measured visually against a standard linear scale and corrected for Lorentz and polarisation factors. Because the crystal used was quite small, no correction was made for either absorption or extinction. The intensity data were initially put on a common scale by using a filming-intensity factor.

6.2.2. Structure Determination and Refinement

A three-dimensional Patterson function for this compound was calculated in the Patterson $P2/m$ group, of higher symmetry than the actual $P2_1/c$ space group to which the crystals belong. Twenty sections of the Patterson function were calculated along $[010]$ from $y = 0$ to $y = \frac{1}{2}$. For space group $P2_1/c$ the appropriate Harker line is $(0y\frac{1}{2})$, and the Harker plane is $(x\frac{1}{2}z)$. The majority of peaks in the Patterson are located in this $(x\frac{1}{2}z)$ plane and in the plane (xOz) . The Patterson section with $y = 0$ is shown in Fig. 6.1. The peaks quoted in this discussion are labelled numerically on this figure.

Along the Harker line $(0y\frac{1}{2})$, there is only the one peak at the location with $y = \frac{1}{2}$. Solution of the equation $\frac{1}{2} \pm 2y = \frac{1}{2}$ gives values of $y = 0$ or $\frac{1}{2}$, and suggest that the majority of the scattering matter in real space lies in these two planes. Because there are two molecules per unit cell, the

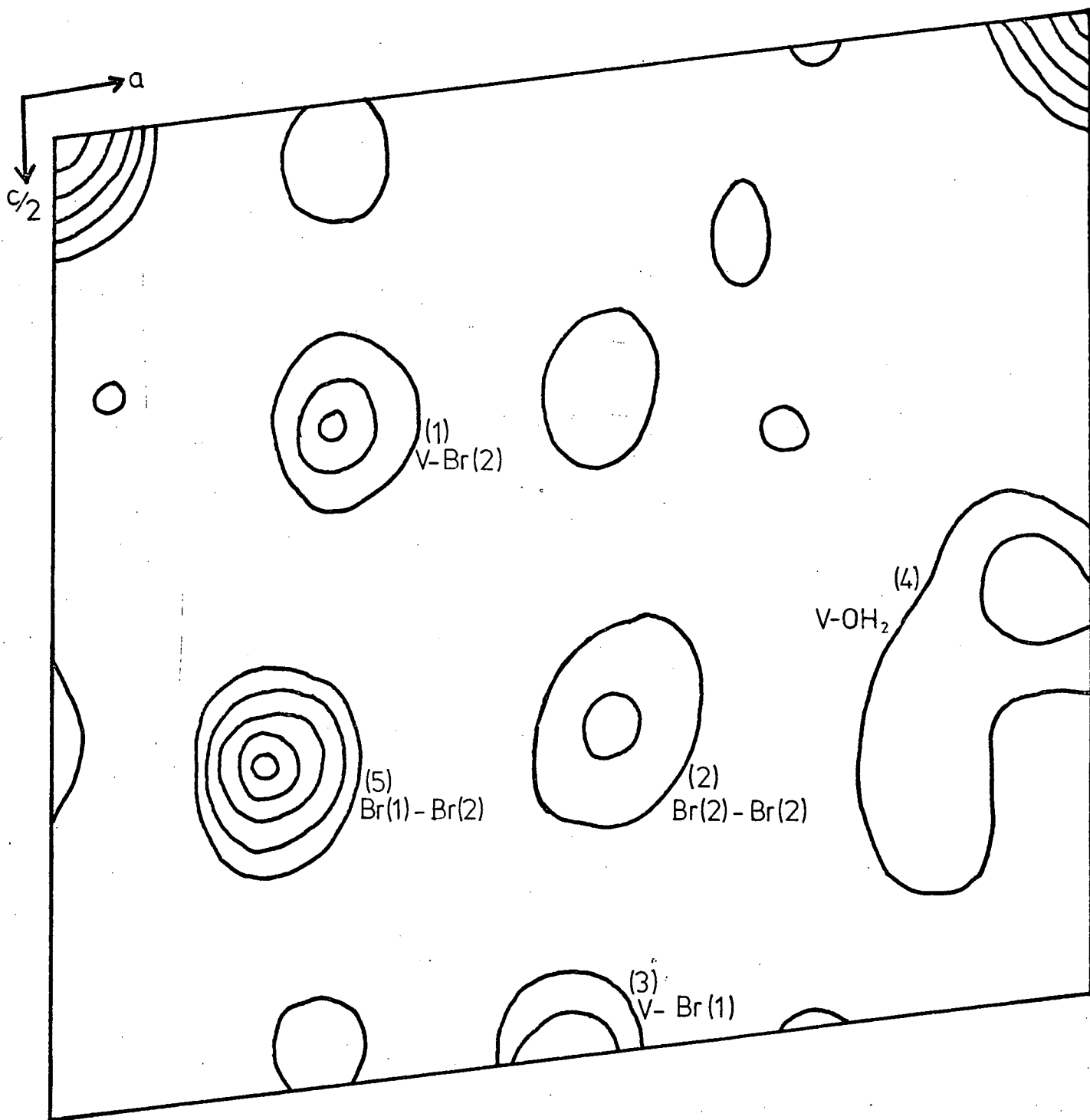


Fig. 6.1

PATTERSON SECTION $y=0$
 $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$

vanadium atom can arbitrarily be taken to occupy the centres of symmetry (0,0,0) and (0,1/2,1/2). The two possible non-bonded bromide ions can then be assigned to one of the other available two-fold positions. The most likely of these positions are at (1/2,0,1/2) and (1/2,1/2,0) and this is confirmed by a large Br-Br vector at (0,1/2,1/2), and a V-Br vector at position (3), ($\frac{1}{2}0\frac{1}{2}$).

The only large interatomic vector within 3.0 Å of the origin, (1), can be attributed to a vanadium bonded-bromine interaction and this is confirmed by the appropriate Br-Br vectors at (2) and (5). From this, the bromine ligands can be located in a general four-fold (x,y,z) position with y approximately equal to zero. This partial model showed a marked similarity to the structure of the iron compound⁸³, $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ which, however, crystallizes in space group C2/m with $z = 2$. By analogy with the Fe structure it was expected that the bromine ligands would lie in the (010) plane, and that the water ligands would occupy symmetrical positions parallel to this plane. The change in space group from C2/m to $P2_1/c$ could then be attributed to the larger bromine ligands distorting the complex ion, and lying slightly out of the (001) plane, a position untenable in C2/m. This assumption turned out to be only partially correct, as repeated attempts to refine the structure based on an $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ type model terminated at R = 24%. Closer examination of the Patterson showed, however, that the V-Br vector did in fact lie out of the (010) plane by an appreciable amount, thus giving a model with the complex ion tilted at an angle to this plane.

As mentioned above refinement was initially attempted on a model derived from the $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ structure. When this proved unsuccessful a fresh start was made with a model based only on the positions of the V and Br atoms derived from the Patterson. From this model, structure factors corresponding to the observed reflections were calculated and Fourier and difference Fourier syntheses carried out. From these it was possible to locate the oxygens of the water ligands and of the waters of crystallization.

ion. Initial structure factor calculations on this complete model gave $R = 24\%$. The refinement then proceeded through several full-matrix least-squares cycles, varying first the layer scale factors and atomic coordinates and then including isotropic thermal parameters in the refinement cycle, giving $R = 17\%$.

At this stage, however, it was noticed that the R-factor for the layer with $k = 4$ was 29% while those for the other four layers were 15%, 16%, 18% and 14% respectively. Re-examination of the films of the fourth level data showed distortion of the spots which could indicate the possibility of crystal decomposition. For this reason and because of the poor residual factor of the data from this level, these reflections were deleted from the refinement process. Further least-squares refinement on the remaining four levels of data gave an R-factor of 15%.

As discussed above, problems had been encountered in crystal selection because of twinning and decomposition. The one crystal that was possible to mount and collect intensity data from, gave diffraction spots of differing shape on different parts of the films. Initial intensity measurements did not fully allow for corrections to be made to account for this and were confined to data on one side of each film. When the structure failed to refine below $R = 15\%$ the intensity data were re-examined. As discussed in Section 1.3.5 it is possible to correct for varying spot size and for α, β splitting at high angles. For the other compounds discussed, correction for varying spot size had not been considered necessary.

For this $VBr_3 \cdot 6H_2O$, however, it was decided to remeasure the data. This time, two sets of data, one from each side of the films, were measured and corrections made for spot length where the reflections were elongated. These data were averaged out, recorrected for Lorentz and polarisation factors and subjected to several further cycles of full-matrix least-squares refinement. The last cycle based on 372 reflections

for hnl ($n = 0-3$) layers gave a residual $R = 11\%$.

Since the shifts in parameters were within the standard deviations, and there were no anomalies in a Final Fourier and Difference Fourier synthesis, this was considered to be a satisfactory completion of the structure determination. As a matter of completeness the Patterson function was re-examined and interatomic peaks verified for all Br - other atom interatomic vectors and in most cases for V - other atom vectors. Some of these are shown above in Fig. 6.1.

Final atomic and thermal parameters are listed in Table 6.3. Some distances and angles are given in Table 6.4, and a comparison of F_{obs} and F_{calc} is given in Appendix 3 Table A.3.13.

The standard deviations attached to atomic coordinates, thermal parameters and bond lengths and angles, are a measure of the consistency of the data set. They do not take into account errors in cell dimensions or intensity data measurement.

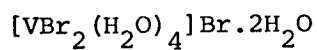
6.2.3. Description of the structure

Fig. 6.2 is a drawing of the unit cell in projection down $[010]$. The Fourier section with $y = 0$ is shown as Fig. 6.3. The vanadium atoms are located at $(0,0,0)$ and $(0,1/2,1/2)$ and are surrounded by six ligands, two of which are bromine atoms trans to one another and the other four are water molecules, the whole forming a distorted octahedral environment around the central metal. The distortion from tetragonal D_{4h} symmetry is small, the Br-V-OH₂ and H₂O-V-OH₂ bond angles differing 3° or less from 90° and the two H₂O-OH₂ distances being nearly equal. Dimensions in the complex ion are also shown in Table 6.4.

The overall arrangement of the $[VBr_2(H_2O)_4]^+$ ions and the remaining bromide ions and water molecules is as illustrated in Fig. 6.2. The centres of the two complex ions per unit cell are located in equivalent

TABLE 6.3

Fractional Atomic coordinates and Isotropic Thermal Parameters



(Standard deviations in parenthesis)

Atom	Position	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$	$B(\sigma_B)$
V	2(a)	0.0	0.0	0.0	1.05(2)
Br(1)	2(d)	0.50	0.0	0.50	1.71(1)
Br(2)	4(e)	0.2812(1)	-0.0239(1)	0.1615(1)	1.97(1)
OH ₂ (1)	4(e)	0.8048(5)	-0.0199(8)	0.3016(3)	1.91(6)
OH ₂ (2)	4(e)	0.1905(6)	0.1286(8)	-0.0948(3)	2.16(9)
OH ₂ (3)	4(e)	-0.0729(6)	0.2674(8)	0.0602(3)	2.58(9)

TABLE 6.4

Distances and Angles

(Standard deviations in parenthesis)

Complex ion	
V-Br (2)	2.539 (1) Å
V-OH ₂ (2)	1.967 (4) Å
V-OH ₂ (3)	1.977 (5) Å
Br (2)-OH ₂ (2)	3.298 (2) Å
Br (2)-OH ₂ (3)	3.313 (3) Å
H ₂ O (2)-OH ₂ (3)	2.747 (7) and 2.828 (5) Å
< Br (2)-V-OH ₂ (2)	93.2 (1) °
< Br (2)-V-OH ₂ (3)	93.5 (1) °
< H ₂ O (2)-V-OH ₂ (3)	88.3 (2) °
Other Closest approach distances	
Br (1)-OH ₂ (1)	3.287 (2)
Br (1)-OH ₂ (2)	3.273 (4)
Br (1)-OH ₂ (3)	3.150 (4)
Br (2)-OH ₂ (1)	3.334 (5)
H ₂ O (1)-OH ₂ (2)	2.644 (3)
H ₂ O (1)-OH ₂ (3)	2.675 (5)

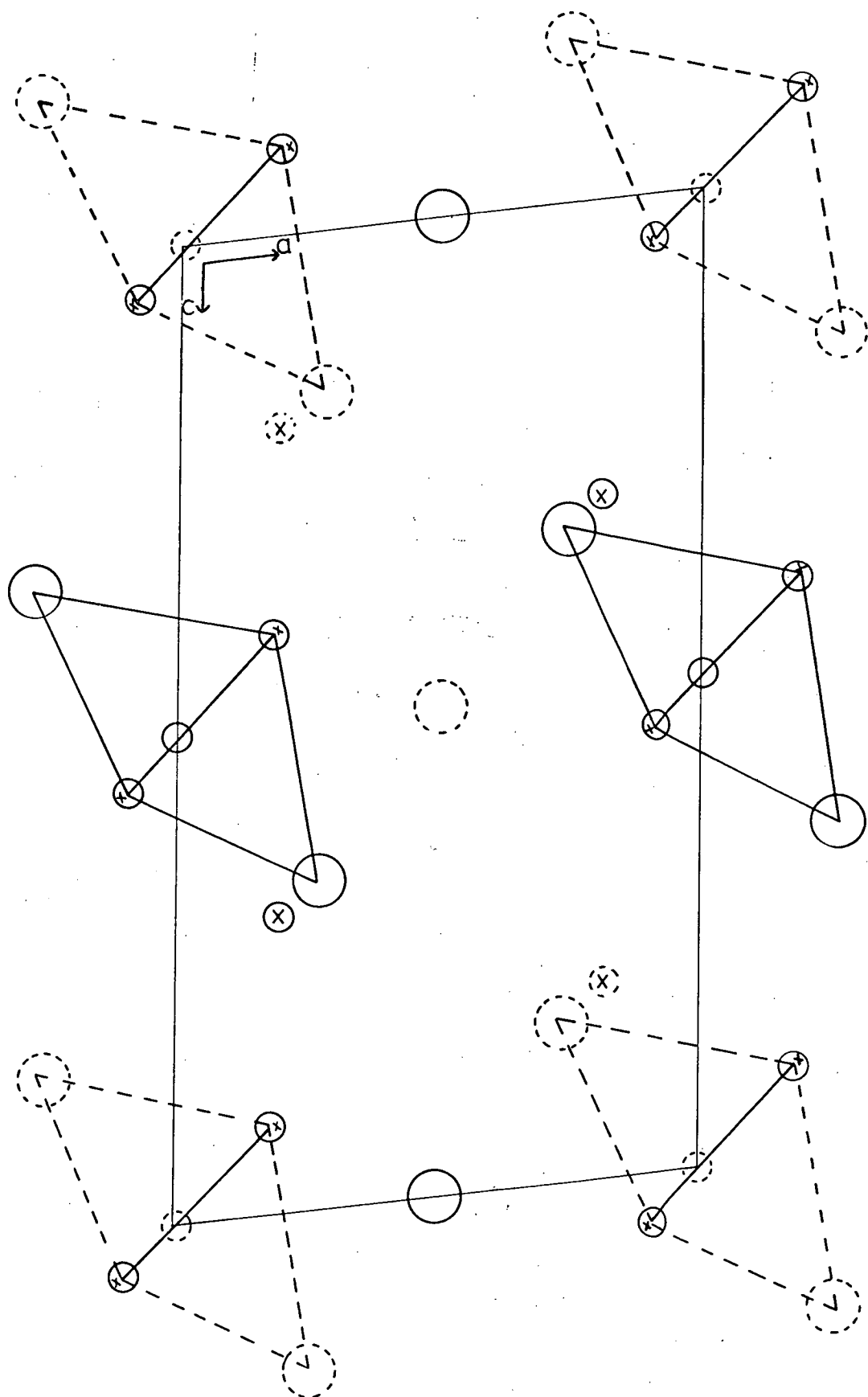
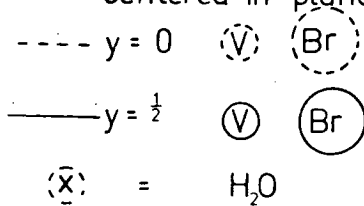


Fig. 6.2 $[\text{VBr}_2(\text{H}_2\text{O})]\text{Br} \cdot 2\text{H}_2\text{O}$ [010] Projection
centered in plane



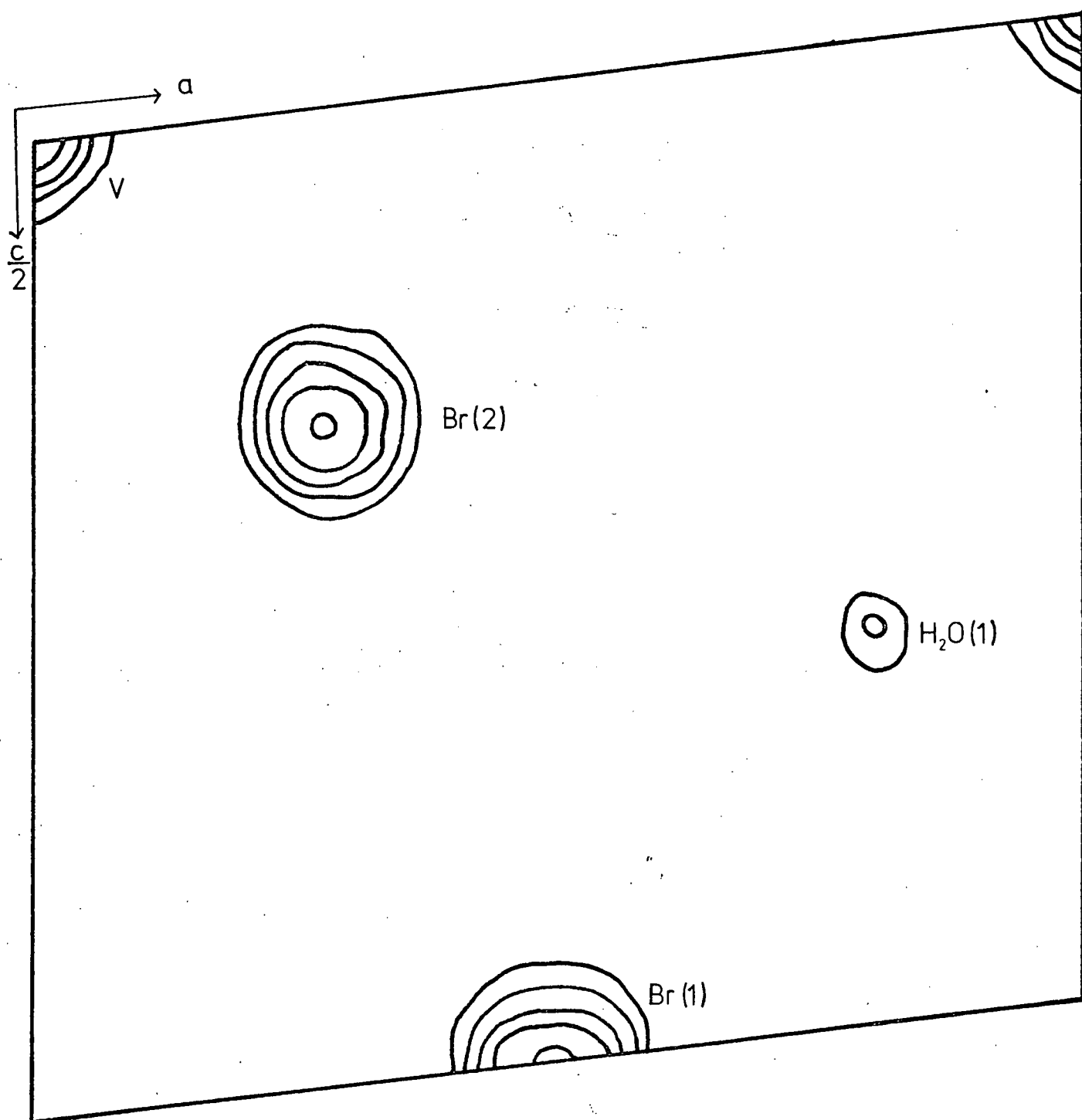


Fig. 6.3 FOURIER SECTION WITH $y=0$ $[\text{VBr}_2(\text{H}_2\text{O})_4] \cdot \text{Br} \cdot 2\text{H}_2\text{O}$

positions (0,0;0) and (0,1/2,1/2). The Vr-V-Br axes are inclined at an angle of approximately 6° from the perpendicular to the b-axis, and make an angle of approximately 60° with the a-axis. The ligand oxygens do not occupy symmetrical locations parallel to the (010) plane, but rather occupy general positions that enable the complex ion to be tilted away from this symmetrical arrangement as adopted by $[\text{FeCl}_2(\text{H}_2\text{O})_4]^+$ ions in $[\text{FeCl}_2(\text{H}_2\text{O})_4] \cdot \text{Cl} \cdot 2\text{H}_2\text{O}^{83}$. The two remaining bromide ions are fixed in a two-fold location (1/2,0,1/2) and (1/2,1/2,0). The four oxygens of the waters of crystallization occupy a general (x,y,z) position located just above and below the planes with $y = 0$ and $y = \frac{1}{2}$.

Each bromide ion is surrounded by a distorted octahedron of six water molecules; two of these, with $\text{Br}-\text{OH}_2 = 3.150 \text{ \AA}$ are waters not bonded to V atoms and four with $\text{Br}-\text{OH}_2 = 3.273$ and 3.287 \AA , are water ligands one from each of four different complex ions see Fig. 6.4(a). These four water molecules link the complex ions by hydrogen bonds to free water molecules, the $\text{H}_2\text{O}-\text{OH}_2$ distances being 2.644 and 2.675 \AA . This H -bonding environment is shown in Fig. 6.4(b), and some H-bond and close approach distances are listed above in Table 6.4.

The bromide ions lie mid-way between octahedra in the (010) plane, the closest Br(ion)-Br(ligand) distances being 8.2 \AA approximately in the plane and 6.4 \AA to the octahedra centered in the plane distance $y = \frac{1}{2}$ away. Thus the bonding between layers of complex ions in planes along the c-axis is presumably both electrostatic between $[\text{VBr}_2(\text{H}_2\text{O})_4]^+$ and Br^- ions and strengthened by H-bonding as discussed above. Therefore the compound should be formulated as $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$, trans- dibromotetraaquovanadium(III) bromide dihydrate.

Having thus determined the crystal structure of $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$, a re-examination was then commenced of the data obtained for $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ in an attempt to solve the possible twinning problem.

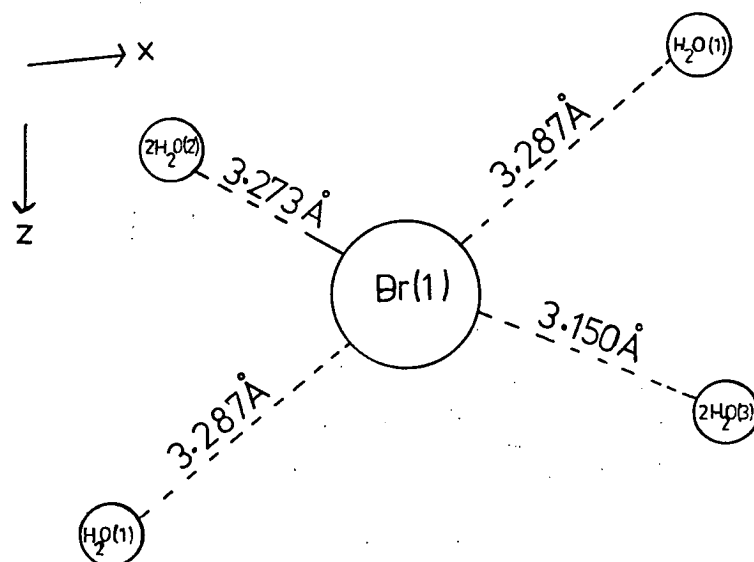


Fig. 6.4 (a) Projection on [010] Br(1) environment
(Bromine surrounded by distorted octahedron
of water molecules)

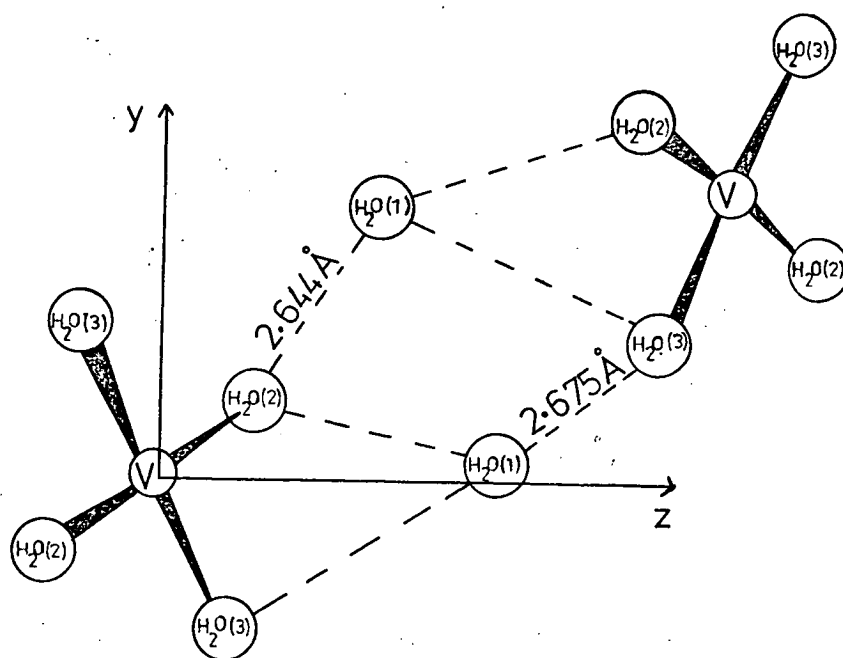


Fig. 6.4 (b) $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$
Possible H-bonding environment viewed down
the x-axis.

6.3. The crystal structure of $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$

6.3.1. Experimental

The sample used was prepared by Podmore⁶¹ from vanadium(III) chloride solution by evaporation and cooling. The green crystals were extremely unstable in air and moisture. It was possible to select apparent single crystals under nujol and mount them in a sealed capillary in a similar manner to that employed for $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$. As discussed in Section 6.1 preliminary Weissenberg photographs taken about the monoclinic b-axis indicated a unit cell with a c-axis approximately twice that in the bromine compound. The absence of reflections for $0k0$ with $k = 2n+1$ suggested the monoclinic space group $\text{P2}_1/\text{m}$ ⁹.

These cell dimensions were refined by least-squares methods on powder data collected on a Philips powder diffractometer using KCl as an internal calibrant. The density measured by the gradient tube technique was 1.65 g/cc. The volume of the unit cell thus required four molecules per unit cell giving a calculated density of 1.79 g/cc. This cell has dimensions $a = 6.430$, $b = 6.439$ and $c = 23.802 \text{ \AA}$, $\beta = 98.8^\circ$

Preliminary Weissenberg photographs also showed very regular spot sizes and shapes and because of the possibility of crystal decomposition 427 non-integrated X-ray intensity data were collected for levels hnl ($n = 0-4$) and recorded photographically on 4-film packs using Cu K_α radiation. The intensities were measured visually against a standard linear scale and corrected for Lorentz and polarisation factors. Corrections were not made for absorption or extinction.

Using values of F_{obs}^2 from this process a three-dimensional Patterson function was calculated in the Patterson group $\text{P2}/\text{m}$ for sections between $y = 0$ and $y = \frac{1}{2}$ with intervals of $1/40$.

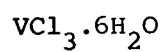
6.3.2. Structure Determination and Refinement

The detailed interpretation of the Patterson function will not be discussed here because this did not lead to the structure. Structural models obtained from the Patterson were, however, used for several attempted structure determinations but the best of these did not refine below a residual factor of $R = 24\%$. At this stage the structure analysis was abandoned in favour of the bromine compound discussed above. (Section 6.2).

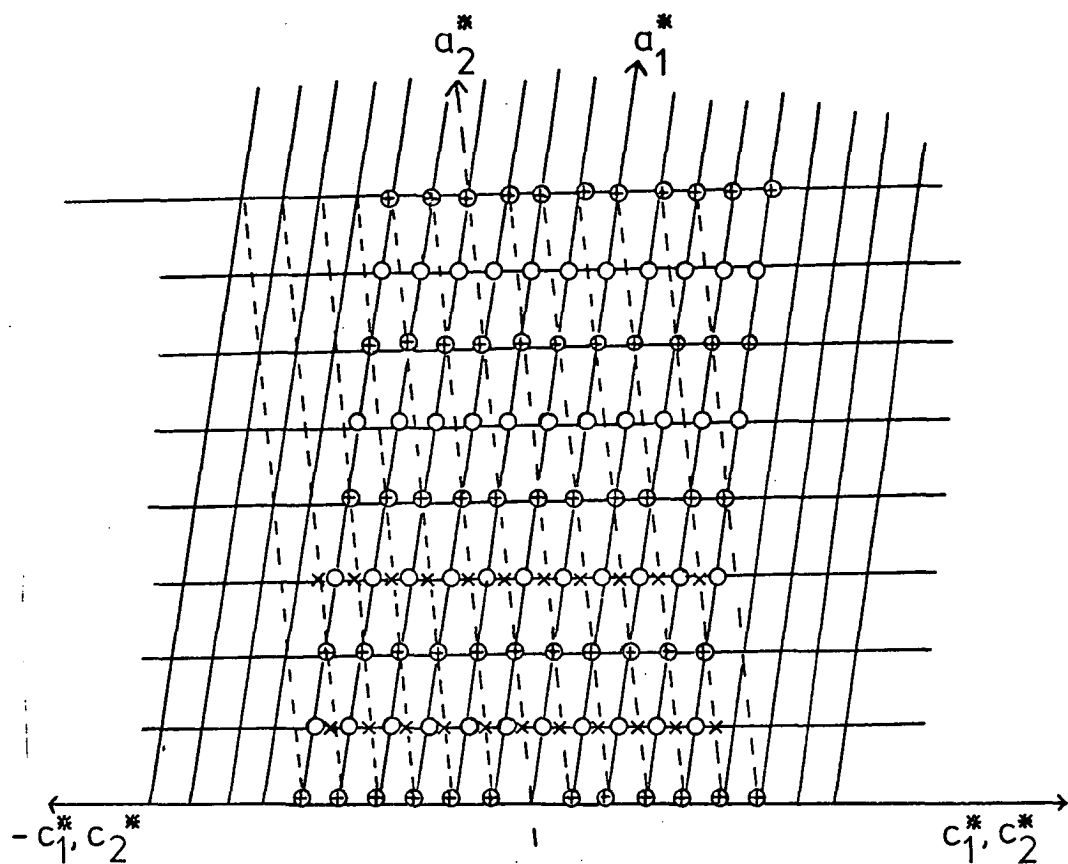
On completion of the structure of $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$ in space group $\text{P2}_1/\text{c}$, attention reverted to the chlorine compounds. The powder data for $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ are similar to those found for the bromine compound, and it was, in fact, found that the powder data of $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ could be indexed and refined for a cell with half the c dimension in space group $\text{P2}_1/\text{c}$. (Table 6.5). This suggested that $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ and $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$ are isomorphous. This smaller cell required two molecules per unit cell. Some form of twinning was suspected and the Weissenberg data were examined to see if it were possible to isolate the data from a single member of the possible twinned crystal. Idealized polar plots of the reciprocal lattice of levels $h0l$ and $h1l$ are shown as Figs. 6.5(a) and 6.5(b). A plot of $h1l$ is representative of all levels with $n > 0$.

For the plot of level $h0l$ a grid can be drawn which relates to a cell of dimensions $a = 6.430$, $b = 6.439$, $c = 11.901 \text{ \AA}$, and $\beta = 98.8^\circ$, with the absence pattern corresponding to $\text{P2}_1/\text{c}$.

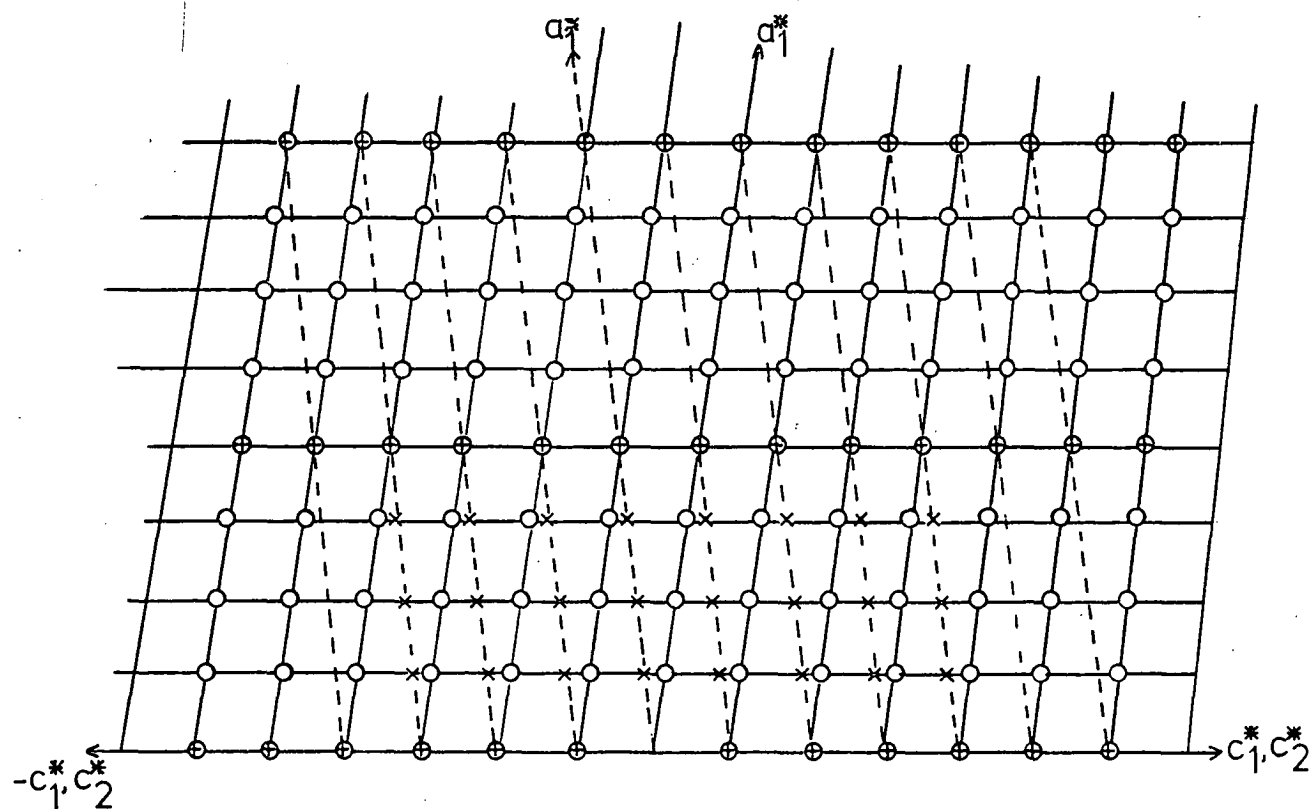
For convenience this grid will be regarded as resulting from crystal (1) and is illustrated by unbroken lines through reflections marked with a small circle. Using a common c^* reciprocal axis, another grid can be drawn for crystal (2) through the remaining unindexed reflections, but with the axis at an angle of 13.9° to the negative a^* axis of crystal (1). Reflections that can be attributed to the lattice of crystal (2) are marked with crosses, while reflections common to both grids are shown as circles

Powder Data⁶¹

$\sin^2 \theta_{\text{obs}}$	$\sin^2 \theta_{\text{calc}}$	Index
146.6	146.8	1 0 0
172.2	171.6	0 0 -2
185.1	186.0	0 1 1
271.8	270.0	1 0 -2
309.3	308.7	1 1 -1
357.6	357.2	1 1 1
527.3	529.1	0 1 3
572.2	572.4	0 2 0
666.4	662.3	2 0 -2
738.2	738.0	1 2 -1
742.8	744.0	0 2 -2
858.8	856.4	2 0 2
930.9	930.3	1 0 4
1237.9	1241.0	1 1 -5
1259.8	1258.7	0 2 -4
1464.5	1465.6	3 1 0
1483.6	1483.7	1 1 5
1546.2	1545.4	1 0 -6

Fig. 6.5 (b) $h1l$

○ strong twin (1)
 × weak twin (2)
 ⊙ common reflections

Fig. 6.5 (a) $h0l$

Twinned Reciprocal Lattice $[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$

superimposed on crosses, and the lattice for crystal (2) shown as broken lines. It can be seen that both grids satisfy the absence of reflections for $\ell = 2n+1$. Reflections with $h = 0, \pm 4$ and ± 8 are common to both lattices.

On the polar plot of the $h1\ell$ layer two similar grids can be sketched in a comparable manner, corresponding to reflections from crystals (1) and (2). Here it can be seen that reflections with h even are common to both lattices with the lack of systematically absent reflections satisfying the space group $P2_1/c$.

Thus the crystals can be considered as being twinned across the (010) plane such that their reciprocal lattices share b^* and c^* axes, with the a^* axes of each twin oriented at $2\beta^* = 162.4^\circ$ to one another. This has the effect of removing an extinction due to the glide-plane of the single crystal in space group $P2_1/c$ and giving the twinned lattice the higher symmetry of $P2_1/m$. It was fortunate that the superposition of one crystal lattice on the other is not exact and it became possible to resolve the reciprocal lattices from one another. This made it a relatively simple matter to draw appropriate nets for the lattices of each twin, and to record the reflections unique to one of the crystals. Dimensions of this smaller unit cell are given in Table 6.6.

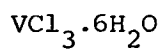
An extensive discussion on twinning of crystals is given by Buerger in the book "Crystal-Structure Analysis"³, and this provided the theoretical basis for the twin resolution discussed above.

The reflections corresponding solely to the strong twin, crystal (1) were extracted and corrected for Lorentz and polarisation factors. No correction was made for absorption. Out of the 427 reflections from the twinned material this made available 126 unique single crystal reflections for the structure refinement process.

Because of the similarity of powder data and unit cell dimensions it

TABLE 6.6

Crystallographic Data



a	$6.430 \pm 0.004 \text{ \AA}$
b	$6.439 \pm 0.004 \text{ \AA}$
c	$11.901 \pm 0.006 \text{ \AA}$
β	$98.8 \pm 0.1^\circ$
d_{calc}	1.77 g/cc.
d_{obs}	1.65 g/cc.
Systematic Absences	$\underline{h}\underline{o}\underline{l}: \underline{l} = 2n+1$
Space Group	$\underline{O}\underline{k}\underline{O}: \underline{k} = 2n+1 \text{ } P2_1/c$
Axis of Data Collection	\underline{b}
Observed Reflections	126 corresponding to strong twin (from 427 reflections from twinned pair).

was presumed that the chlorine and bromine compounds were isomorphous. Therefore a model derived from the structure of the bromine compounds was adapted to account for the smaller V-Cl as compared to V-Br bond lengths, and this model was used for refinement of the $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ structure.

Structure factors were calculated corresponding to the 126 observed reflections used. A comparison of observed versus calculated structure factors gave an initial residual factor of $R = 20\%$. Fourier and difference Fourier syntheses based on this data showed no reasons for changing the structure. Accordingly, full matrix least-squares refinement on the structure factors proceeded through several cycles, varying first the coordinates and scale factors and then including isotropic thermal parameters. The shifts in parameters in the final cycle were inside the standard deviations, giving a final R factor of 12% . Final Fourier and difference Fourier maps showed no anomalies.

It would be possible to calculate the contribution of crystal (1) to each of common reflections on the twinned lattice. This was not done, however, because the 126 reflections used provided over five reflections per variable in the final refinement cycles, and gave satisfactory values to the variable parameters and also for bond lengths and angles which were calculated from them. This was accordingly regarded as the termination of the structure determination. Atomic coordinates and isotropic thermal parameters are listed in Table 6.7.

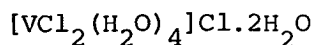
A comparison of F_{obs} versus F_{calc} is given as Table A3. Appendix 3.14.

6.3.3. Description of the Structure

This compound, $[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ is isostructural with that of $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$ discussed in detail in Section 6.2.3. In the distorted octahedral unit of $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ the V-Cl bond length is 2.361 \AA , and the two V-OH₂ bond lengths are 1.961 and 2.024 \AA , values that are consistent with bond lengths found in the other two compounds, $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$ and

TABLE 6.7

Fractional Atomic Coordinates and Isotropic Thermal Parameters



(Standard deviations in parenthesis)

Atom	Position	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$	$B(\sigma_B)$
V	2(a)	0.0	0.0	0.0	1.93(6)
Cl(1)	2(d)	0.50	0.0	0.50	1.43(8)
Cl(2)	4(e)	0.2707(3)	-0.0293(6)	0.1577(2)	3.59(6)
OH ₂ (1)	4(e)	0.7813(8)	0.0097(17)	0.2979(5)	3.44(15)
OH ₂ (2)	4(e)	0.1931(9)	0.1490(14)	-0.0927(5)	3.04(15)
OH ₂ (3)	4(e)	-0.0761(10)	0.2621(12)	0.0656(5)	3.49(16)

$\text{Rb}[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_2\cdot 2\text{H}_2\text{O}$, and the V-OH₂ bond length found in $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br}\cdot 2\text{H}_2\text{O}$. The distortion of the complex ion from tetragonal D_{4h} symmetry is small, with bond angles deviating by less than 4° from 90°. Dimensions in the complex ion are shown in Table 6.8.

The chloride ions, Cl(2), are surrounded by a distorted octahedron of two waters of crystallization with Cl-H₂O = 3.111 Å, and four water ligands with Cl-H₂O = 3.097 and 3.229 Å, one from each of four complex ions.

Like the overall arrangement in $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br}\cdot 2\text{H}_2\text{O}$, the crystal structure of $[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}\cdot 2\text{H}_2\text{O}$ consists of a close-packed array of $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ and Cl^- ions and water molecules, with the bonding between species being electrostatic supported by hydrogen bonding between complex ions through H₂O-OH₂ links. Relevant H-bonded and closest approach distances in the unit cell are also shown in Table 6.8.

TABLE 6.8

Distances and Angles

(Standard and deviations in parenthesis)

Complex ion	
V-Cl (2)	2.361 (2) Å
V-OH ₂ (2)	2.024 (5) Å
V-OH ₂ (3)	1.961 (7) Å
Cl (2)-OH ₂ (2)	3.053 (6) Å
Cl (2)-OH ₂ (3)	2.999 (7) Å
H ₂ O (2)-H ₂ O (3)	2.784 (11) and 2.852 (7) Å
< Cl (2)-V-OH ₂ (2)	92.1 (1) °
< Cl (2)-V-OH ₂ (3)	92.6 (2) °
< H ₂ O (2)-V-H ₂ O (3)	88.6 (2) °
Other closest approach distances	
Cl (1)-OH ₂ (1)	3.229 (4)
Cl (1)-OH ₂ (2)	3.097 (7)
Cl (1)-OH ₂ (3)	3.111 (6)
Cl (2)-OH ₂ (1)	3.015 (10)
H ₂ O (1)-H ₂ O (2)	2.684 (6)
H ₂ O (1)-H ₂ O (3)	2.809 (9)

Chapter 7

Crystal Structures of Vanadium(III) Aqua Chloro Complexes

Discussion

The four crystal structures of V(III) complexes reported in this thesis, and that of $\text{Cs}_2\text{VBr}_5 \cdot 4\text{H}_2\text{O}$ reported jointly with Podmore, have all been shown to contain the trans- $[\text{VX}_2(\text{H}_2\text{O})_4]^+$ ($\text{X} = \text{Cl}, \text{Br}$) complex ion. Similar complex ions have been found in aqua halide compounds of other first row transition metals, and it is, therefore, relevant here to briefly describe the structures of these compounds before discussing structural comparisons.

Dance and Freeman⁸⁴ have reported that $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ should in reality be trans- $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$. This has been confirmed by Morosin⁸⁵. In the structure there are four molecules per unit cell in the monoclinic group, C2/c . The slightly distorted complex ions are linked in chains by hydrogen-bonded "cages" of water molecules and chloride ions. This hydrogen-bonding reinforces the electrostatic attraction between Cl^- and $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ ions. Some crystal structure data for this are given in Table 7.1.

Lind⁸³ has shown the analogous compound $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to be trans- $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$. The compound crystallizes, however, in a different monoclinic space group, C2/m , with only two molecules per unit cell. The packing of slightly distorted $[\text{FeCl}_2(\text{H}_2\text{O})_4]^+$ ions, water molecules and chloride ions suggests strong electrostatic forces between the ions together with hydrogen bonding. Four water molecules form apparent hydrogen-bond bridges between adjacent complex ions and each chloride ion is likewise apparently hydrogen-bonded to six water molecules, two of which are waters of crystallization and the other four are ligands in four different complex ions.

By contrast the non-transition metal Gd forms a coordination compound $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, which has been shown to contain $[\text{Gd}(\text{H}_2\text{O})_6]^{3+}$ and Cl^- ions⁸⁶. The compound crystallizes in space group P2/n with cell dimensions similar to $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as shown in Table 7.1.

TABLE 7.1

Crystallographic Data

	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}^{84}$	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}^{83}$	$\text{GdCl}_3 \cdot 6\text{H}_2\text{O}^{86}$
a (Å)	12.053	11.89	9.651
b (Å)	6.840	7.05	6.525
c (Å)	11.640	5.99	7.923
β (°)	94.2°	100.5°	93.7°
z	4	2	2
Space Group	C2/c	C2/m	P2/n
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}^{87}$	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}^{88}$	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}^{89}$
a	10.30	10.23	9.90
b	7.06	7.05	7.15
c	6.67	6.57	6.10
β	122.3°	122.2°	94.0°
z	2	2	2
Space Group	C2/m	C2/m	C2/m

In the 2^+ oxidation state, structures of other similar coordination compounds have been reported. Two of these compounds $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}^{87}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}^{88}$ contain trans- $[\text{MCl}_2(\text{H}_2\text{O})_4]^\circ$ (M = Co or Ni) units. Crystallographic data for these are also shown in Table 7.1. The compounds have similar structures to $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}^{83}$ and crystallize in the same space group. A brief structural description⁸⁷ of for example, $[\text{CoCl}_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ is that adjacent sheets of "cage" linked octahedra are held together by weak hydrogen

bonds, between one hydrated water molecule and a ligand water from each of two complex ions.

The structures of these two compounds are in contrast to that of the non-transition metal compound $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. For this compound Andress and Gundermann⁸⁹ show that there is a six-fold coordination of water ligands around the metal with no metal-chlorine bonding. That is, the compound should be formulated as $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}_2$.

Structural Comparisons

The two isomorphous halides (reported in Chapter 6) which can be formulated as $[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ and $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$ have similar structures to $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ⁸³. The monoclinic space group adopted by $[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ is $\text{P}2_1/\text{c}$, rather than $\text{C}2/\text{m}$ as for the iron compound, but both have in common two molecules per unit cell. In the iron compound the Cl-Fe-Cl axis lies in the plane with $y = 0$, but the Cl-V-Cl axis is inclined at an angle of approximately 6° to this plane in the vanadium complex. This is somewhat more related to the Cl-Cr-Cl axis which lies at an angle to the plane containing the Cr atoms in $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ⁸⁴, although this chromium compound crystallizes in a different space group again namely, $\text{C}2/\text{c}$, with $z = 4$. All these compounds which do not contain M^{1+} cations have in common the hydrogen-bonded "cages" of water molecules and Cl^- or Br^- ions which link the complex ions in chains. It is interesting that three compounds of similar stoichiometry and only differing in the type of M^{3+} atom should crystallize in three different monoclinic space groups.

In this context, it has been shown by Podmore⁶¹ that $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ has a similar powder pattern to $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$, both of which are different from the patterns obtained from $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. It can be expected, therefore, that the structure of $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ is isomorphous with that of $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$. The powder data for $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ is similar to that reported by Gardiner⁹⁷.

The structures of the two isomorphous caesium compounds, $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$ and $\text{Cs}_2[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br}_3$, (Chapter 4) can also be compared with that of $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$. These three compounds crystallize in space group C2/m with $z = 2$. In the structure of the vanadium compounds, two non-bonded halide ions occupy positions analogous to free water molecules in the iron compound. The caesium ions in the V(III) structures are located in the (010) plane between the ligand halogens and the free halide ions. This gives rise to a much greater a -axis and a slightly expanded c -axis compared with those of the iron compound. The degree of apparent hydrogen-bonding in the V(III) compounds is much less than in the iron compound, because of the absence of waters of crystallization. This factor also precludes the H-bonded "cages" of water molecules reported for $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$, and postulated for $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$.

The other V(III) compound studied $\text{RbVCl}_4 \cdot 6\text{H}_2\text{O}$ (Chapter 5) has the same number of atoms in the molecule as $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$, but the two compounds are of differing stoichiometry. The rubidium compound which should be formulated as $\text{Rb}[\text{VCl}_2(\text{H}_2\text{O})_4] \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$, is the only one of this set which crystallizes in orthorhombic symmetry with space group Cccm , and $z = 4$.

The presence of waters of crystallization in the rubidium compound suggests a greater degree of hydrogen-bonding than in $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$, and this indeed appears to be the case. In fact, the distance of closest H-bond approach of 2.56 \AA for $\text{H}_2\text{O}-\text{OH}_2$ in the rubidium compound is smaller than that found in any of the other compounds. The orthorhombic symmetry appears to arise because the packing of the Rb^+ ions and the arrangement of the other species with respect to one another, imposes higher symmetry of the overall structure than is the case for the other compounds.

Bond Lengths

The bond lengths in the complex ions of type $[\text{VX}_2(\text{H}_2\text{O})_4]^+$ ($\text{X} = \text{Cl}, \text{Br}$), in compounds discussed in Chapters 4, 5 and 6 are shown in Table 7.2. The

TABLE 7.2

Bond lengths in $[\text{MX}_2(\text{H}_2\text{O})_4]^+$ ($\text{X} = \text{Cl}, \text{Br}$) ($\text{M} = \text{V}, \text{Cr}, \text{Fe}$) ions.

(Angstroms)

(Standard deviations in parenthesis)

	M-X	M-H ₂ O(1)	M-H ₂ O(2)
$\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$	2.361(2)	1.983(5)	-
$\text{Rb}[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	2.367(1)	2.003(4)	2.044(8)
$[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$	2.361(2)	1.961(7)	2.024(5)
$\text{Cs}_2[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br}_3$ ⁶¹	2.497(1)	2.060(7)	-
$\text{V}[\text{Br}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$	2.539(1)	1.967(4)	1.977(5)
$[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ⁸⁴	2.289 ± 0.001	2.004 ± 0.004	2.066 ± 0.004
$[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ⁸³	2.30 ± 0.02	2.07 ± 0.02	-

average values for the bond lengths as calculated from all five structures are, $\text{V-Cl} = 2.363 \pm 0.004 \text{ \AA}$, $\text{V-Br} = 2.52 \pm 0.02 \text{ \AA}$ and $\text{V-OH}_2 = 2.01 \pm 0.04 \text{ \AA}$.

The V-Br bond lengths found in $\text{Cs}_2[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br}_3$ and $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$ are in close agreement.

The V-Cl distance lies between that reported in VCl_3 ⁹⁸, where $\text{V-Cl} = 2.45 \text{ \AA}$ and in $\text{VCl}_3(\text{NMe})_2$ ⁹³, where $\text{V-Cl} = 2.239 \text{ \AA}$. Direct comparisons cannot be made between these, as the environment around the V(III) ion is different in each case. Comparisons can be made with bond lengths reported in the structures of $\text{Cr}[\text{Cl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ⁶⁴ and $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ⁶³, the bond lengths being shown above in Table 7.2. The average V-Cl bond length of 2.363 \AA is larger than both $\text{Cr-Cl} = 2.289 \text{ \AA}$ and $\text{Fe-Cl} = 2.30 \text{ \AA}$, and when it is considered that Cr-Cl in CrCl_3 is 2.35 \AA and Fe-Cl in FeCl_3 is 2.38 \AA , the relative magnitudes of M-Cl bonds in $[\text{MCl}_2(\text{H}_2\text{O})_4]^+$ ions follows the same pattern. This is clearly shown in Table 7.3.

TABLE 7.3

Comparison of M-Cl bond lengths (Angstroms)

(M = Ti, V, Cr, Fe)

	Ti-Cl	V-Cl	Cr-Cl	Fe-Cl
MCl_3	2.47^{99}	2.45^{98}	2.35^{100}	2.38^{101}
$[\text{MCl}_2(\text{H}_2\text{O})_4]^+$	-	2.363	2.289^{64}	2.30^{63}

This would suggest that the degree of ionic bonding in the complex ions is less than in the MCl_3 compounds, with orbital overlap in the M-Cl bonds of the complex ions having the effect of reducing the M-Cl bond lengths.

The V- H_2O distance averaged for the five compounds, is consistent with the average value of $2.00 \pm 0.02 \text{ \AA}$ calculated from the three compounds containing $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ ions, and the value $2.02 \pm 0.004 \text{ \AA}$ obtained from the two compounds containing $[\text{VBr}_2(\text{H}_2\text{O})_4]^+$ ions.

The M- OH_2 bond lengths in $[\text{MCl}_2(\text{H}_2\text{O})_4]^+$ complex ions do not show such a clear pattern as the M-Cl bond lengths. The average values are V- $\text{OH}_2 = 2.01 \pm 0.04 \text{ \AA}$; Cr- $\text{OH}_2 = 2.055 \pm 0.005 \text{ \AA}$ ⁸⁴ and Fe- $\text{OH}_2 = 2.07 \pm 0.02 \text{ \AA}$ ⁸³. On the M-Cl trends it would be expected that the V- OH_2 should be $> 2.07 \text{ \AA}$ but none of the V- OH_2 bond lengths exceeded 2.05 \AA . As mentioned in Chapter 4 the determination of water positions produced some problems and structure analyses of greater accuracy could give V- OH_2 bond length slightly different to that found in this work.

Symmetry of the complex ions

In the five V(III) compounds studied, the complex ions all show distortion from tetragonal D_{4h} symmetry. A comparison of the bond lengths and bond angles in the complex ions is shown in Figs. 7.1 and 7.2. In most cases the X-V- OH_2 angles are less than the H_2O -V- OH_2 angles

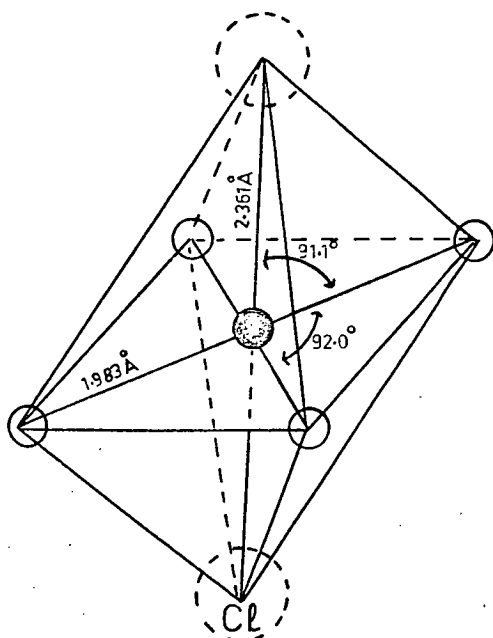
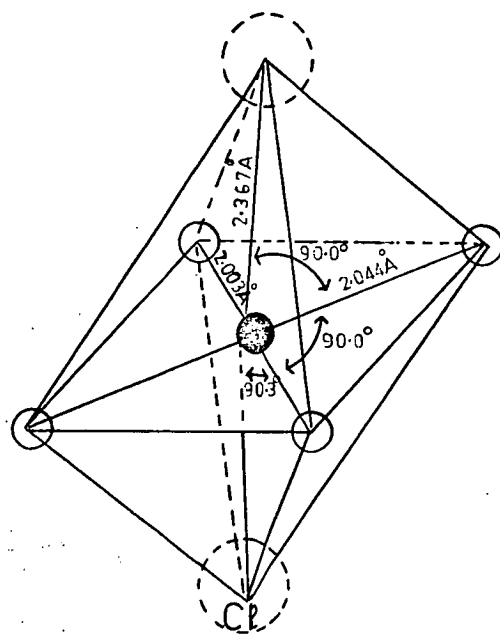
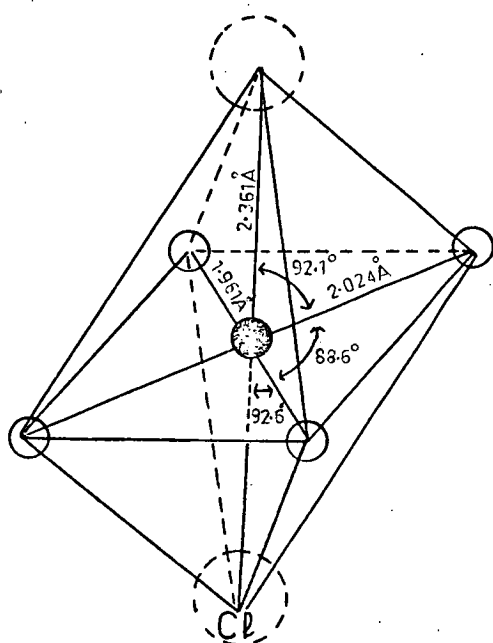
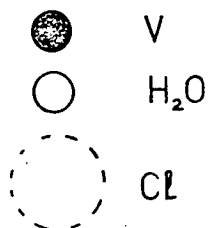
(a) $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$ (b) $\text{Rb}[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (c) $[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$

Fig. 7.1

A comparison of $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ octahedral coordination in three compounds



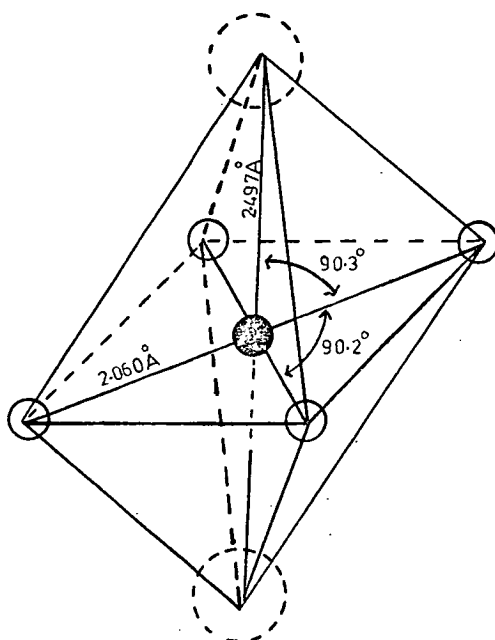


Fig. 7.2(a)

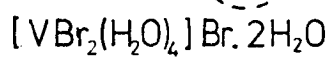
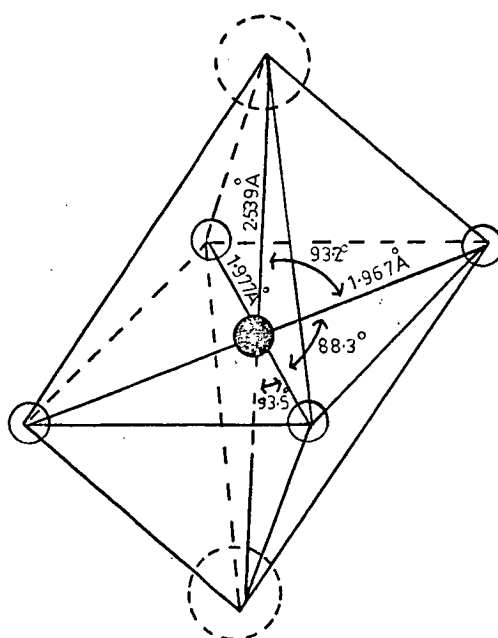
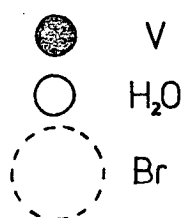
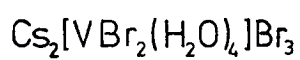


Fig. 7.2(b)

$[\text{VBr}_2(\text{H}_2\text{O})_4]^+$ octahedral coordination in two different compounds

with deviations being within $\pm 4^\circ$ of 90° in all cases. It might be expected that the distortion in the bromine complexes would be greater, because of the size increase of bromine ligands over chlorine. The angular distortions are, however, very close to those of the chlorine complexes, the only difference being that the $\text{H}_2\text{O}-\text{OH}_2$ distances in the bromine compounds are slightly longer than those in the chlorine compounds. The distortion of the octahedral complex ion symmetry is comparable to that found in $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ⁶⁴ and $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ⁶³. While the X-ray crystallographic data show appreciable distortion of the $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ octahedral ions there is no direct evidence to support a lesser distortion for compounds containing the ~~$[\text{VCl}_5(\text{H}_2\text{O})]^-$~~ ^{caesium and rubidium double salts} ions, as postulated by Podmore and Smith⁷⁰. However, an analogy can perhaps be taken with iron compounds of the two types while structures are known. Where the angular distortion in the complex ions in $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ⁶³ and for example $\text{Rb}_2[\text{FeCl}_5(\text{H}_2\text{O})]$ (Chapter 3) is approximately of the same order, the latter compound lies closer to cubic symmetry by virtue of greater equivalence of bond lengths.

It would be of interest, therefore, to determine the crystal structure of the $\text{M}_2^{\text{I}}[\text{VCl}_5(\text{H}_2\text{O})]$ ($\text{M} = \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$) compounds mentioned in Section 3. As well as classifying these compounds into Pnma or Cmcm types, dimensions in the complex ions could prove that there is less distortion in these type of compounds than those containing $[\text{VCl}_2(\text{H}_2\text{O})_4]^+$ ions, thus confirming postulates made from magnetic data⁶¹. Evidence from bond lengths could also provide data on which to develop trends in bond lengths in different types of complex ions and to show there is in fact a decrease in V-Cl bond length in the order $[\text{VCl}_6]^{3-} < [\text{VCl}_5\text{H}_2\text{O}]^{2-} < [\text{VCl}_4(\text{CH}_3\text{COOH})_2]^{1-} < [\text{VCl}_2(\text{H}_2\text{O})_4]^+$.

Ionic Radii

In considering ionic radii of, for example, M^{3+} first row transition elements in octahedral complexes, the traditional approach is to predict a contraction of ionic radii across the group because of increasing effective nuclear charge. This approach requires modification, however, because the non-spherical distribution of d electrons gives rise to imperfect shielding of one d electron by another from the nuclear charge, giving rise to ionic radii which fall below the theoretical values.

For Ti^{3+} the one d electron in t_{2g} lies away from the octahedral ligands, resulting in little shielding between the ligand and Ti^{3+} . This causes the ionic radii to be lower as the ligand is drawn closer to the metal, than would have been the case if the ligands had been spherically shielded. A similar theory applies to V^{3+} and Cr^{3+} where two and three t_{2g} electrons would provide much less shielding than spherically distributed d electrons.

For Mn^{3+} and Fe^{3+} the ground state configurations t_{2g}^3, e_g^1 and t_{2g}^3, e_g^2 have electrons in orbitals along the ligand axes and hence provide more symmetrical screening between the metal and the ligand. Thus the ionic radii would be expected to increase. A similar sequence of decrease then increase of ionic radii would be expected in the second half of the series.

Whereas this type of reasoning has been confirmed for M^{2+} ions there is little experimental data available for M^{3+} compounds from which verification can be made. Wells⁷² gives M^{3+} radii in compounds of the type $A^{III} B^{III} O_3$ where the ionic radius for the d^2 configuration (V^{3+}) is the only one which does not fit the predicted pattern. (Table 7.4).

X-ray structure studies have been made of several compounds of the type MCl_3 and the M-Cl bond lengths calculated are given above in Table 7.3. If the bonding is presumed to be ionic and the radii of the Cl^- ion taken to be 1.81 \AA^{72} , then the M^{3+} ionic radii can be calculated. This gives

TABLE 7.4

 M^{3+} radii

	$A_{M^{III}O}^{III}{}^{72}$	MCl_3	M_2O_3	$[MCl_2(H_2O)_4]^+$ from M-O	$[MCl_2(H_2O)_4]^+$ from M-Cl
Sc	0.686	-	-	-	-
Ti	0.610	0.57^{99}	0.68	-	-
V	0.625	0.64^{98}	0.66	0.604	0.550
Cr	0.608	0.54^{100}	0.62	0.605^{84}	0.479^{84}
Mn	-	-	-	-	-
Fe	0.628	0.57^{101}	0.66	0.607^{83}	0.490^{83}
Co	0.560	-	-	-	-

TABLE 7.5

Bond lengths in M_2O_3 compounds¹⁰² (Angstroms)

	M-O(1)	M-O(2)
Ti_2O_3	2.01	2.08
V_2O_3	1.96	2.06
Cr_2O_3	1.97	2.02
Fe_2O_3	1.91	2.06

values of 0.66, 0.64, 0.54 and 0.57 Å for Ti^{3+} , V^{3+} , Cr^{3+} and Fe^{3+} respectively and these are also shown in Table 7.4. This pattern agrees with the theoretical discussion above, except that the Fe^{3+} radius might have been expected to be somewhat greater.

Crystal structure studies of simple oxides with the formula M_2O_3 ¹⁰², show each metal atom surrounded by six oxygen atoms at the corners of an octahedron, with two different M-O bond lengths (see Table 7.5). If O^{2-} is taken as having a radius of 1.40 Å, then the M^{3+} radii from the longer M-O bonds are 0.68, 0.66, 0.62 and 0.66 Å for Ti^{3+} , V^{3+} , Cr^{3+} and Fe^{3+} respectively. (Table 7.4).

For the tetragonally distorted octahedral complex ions of formula $[\text{MCl}_2(\text{H}_2\text{O})_4]^+$ the bond lengths are listed in Table 7.2. From M-O bond lengths and taking $\text{O}^{2-} = 1.40 \text{ Å}$ ⁷² the ionic radii are 0.604, 0.605 and 0.607 Å for V^{3+} , Cr^{3+} and Fe^{3+} respectively. From M-Cl bond lengths with Cl^- taken as 1.81 Å the values of 0.55, 0.479 and 0.49 are obtained. (Table 7.4).

Conclusion

X-ray crystallographic techniques have been used to study the crystal and molecular structures of some chemically interesting compounds containing pseudo-octahedral complex ions of M(III) transition metals.

The study of thiocyanates of Cr(III) and Mo(III) was complicated by the possible presence of twinning, disorder or superlattice effects. The incomplete structure determinations do, however, provide evidence of metal to nitrogen bonding in the complex ions, and that $K_3[Cr(NCS)_6] \cdot 4H_2O$ and $K_3[Mo(NCS)_6] \cdot 4H_2O$ are isomorphous.

Structures of six compounds of the type $A_2^I[M^{III}Cl_5H_2O]$, with $A = K, Rb, NH_4, \text{ or } Cs; M = Fe \text{ or } Mo$; have been determined. From these it has been possible to calculate bond lengths and angles in the complex ions of the type $[MoCl_5H_2O]^{2-}$ and $[FeCl_5H_2O]^{2-}$. Further, the compounds studied can now be classified as belonging to either the Pnma, $[Rh(NH_3)_5Cl]Cl_2$ or to the Cmc, $Cs_2[RuCl_5H_2O]$ structural types. It appears that there is a limiting central metal M^{3+} ionic radius above which the caesium salts revert to the $[Rh(NH_3)_5Cl]Cl_2$ structure, because of more favourable crystal packing considerations.

Five "green" compounds of V(III), $Cs_2VCl_5 \cdot 4H_2O$, $Cs_2VBr_5 \cdot 4H_2O$, $RbVCl_4 \cdot 6H_2O$, $VBr_3 \cdot 6H_2O$ and $VCl_3 \cdot 6H_2O$, have been shown to contain the slightly distorted octahedral trans- $[VX_2(H_2O)_4]^+$ complex ion. The bonding between species in these compounds is mainly electrostatic, supported to varying degrees by hydrogen bonding between free ions and water molecules, with ligand molecules from the complex ions.

Bond lengths and angles in the complex ions have been calculated. Average values for bond lengths are $V-Cl = 2.363 \pm 0.04 \text{ \AA}$, $V-Br = 2.52 \pm 0.02 \text{ \AA}$ and $V-OH_2 = 2.01 \pm 0.04 \text{ \AA}$. The complex ions show appreciable distortion from D_{4h} tetragonal symmetry.

It is possible to compare the radii of the M(III) species in series of similar compounds, and to show trends across the first row transition metal ions.

In all these structure determinations there are limitations on the accuracy and precision of data. This is brought about by limiting the data collection, mainly because of the extremely unstable nature of some of the compounds studied, and is also inherent in the film collection of X-ray data and in the eye measurement of these data. The standard deviations reported for atomic coordinates, thermal parameters and bond lengths and angles, are those calculated by least-squares methods in the computer programs involved. Thus these deviations represent a measure of the consistency of the data set, and do not take into account errors in cell dimensions or in intensity measurement.

It would be of interest, as a continuation of the research described herein, to determine the structures of several other compounds. For instance, the structures of $A_2^I[VC l_5 H_2 O]$ ($A = K, NH_4, Rb$ or Cs) compounds, could provide evidence to show less distortion in the expected $[VC l_5 H_2 O]^{2-}$ complex ion than in $[VC l_2 (H_2 O)_4]^+$ ions. Bond length data could verify an expected decrease in V-Cl distances in the order $[VC l_6]^{3-} < [VC l_5 H_2 O]^{2-} < [VC l_2 (H_2 O)_4]^+$. The structures of the $A_2^I[VC l_5 H_2 O]$ compounds could also be classified as belonging to either the $Pnma$ or $Cmcm$ types, known for similar compounds of other trivalent metals.

Because the M(III) compounds $[VC l_2 (H_2 O)_4]Cl \cdot 2H_2 O$, $Cr[Cl_2 (H_2 O)_4]Cl \cdot 2H_2 O$ and $[FeCl_2 (H_2 O)_4]Cl \cdot 2H_2 O$ crystallize in different monoclinic space groups with slightly different structures, it would be interesting to determine the structure of the analogous compound $TiCl_3 \cdot 6H_2 O$. Powder data suggests that it is isomorphous with the vanadium compound and this could best be verified from a single crystal X-ray diffraction study. Data from this structure would provide further evidence for trends in properties in similar compounds of first row transition M(III) metals.

REFERENCES

1. Stout, G.H., and Jensen, L.H., "X-Ray Crystal Structure Determination", Macmillan, London, 1968.
2. Lipson, H., and Cochran, W., "The Determination of Crystal Structures", Bell, London, 1968.
3. Buerger, M.J., "Crystal-Structure Analysis", Wiley, New York, 1967.
4. Buerger, M.J., "Elementary Crystallography", Wiley New York, 1963.
5. Buerger, M.J., "X-Ray Crystallography", Wiley, New York, 1942.
6. Buerger, M.J., "Vector Space", Wiley, New York, 1959.
7. Bunn, C.W., "Chemical Crystallography", Oxford University Press, New York, 1961.
8. Woolfson, M.M., "X-Ray Crystallography", Cambridge University Press, Bristol, 1970.
9. International Tables of X-Ray Crystallography, Vol. I., Kynock Press, Birmingham, 1965.
10. International Tables for X-Ray Crystallography, Vol. II, Kynock Press, Birmingham, 1962.
11. International Tables for X-Ray Crystallography, Vol. III, Kynock Press, Birmingham, 1962.
12. Friedrich, W., Knipping, P., and Laue, M., Sitzungsberichte der mathematisch-physikalischen Klasse der Königlich Bayerischen Akademie der Wissenschaften zu Munchen, 1912, 363, reprinted in Naturwiss., 1952, 361.
13. Laue, M., ibid 1912, 363, reprinted in Naturwiss., 1952, 368.
14. Laue, M., Physik. Z., 1913, 14, 1075.
15. Bragg, W.L., Proc. Roy. Soc. London, 1913, 88, 428.
16. Patterson, A.L., Phys. Rev., 1934, 46, 372.
17. Patterson, A.L., Z. Krist., 1935, 90, 517.
18. Harker, D., J. Chem. Phys., 1936, 4, 381.
19. Buerger, M.J., J. Appl. Phys., 1946, 17, 579.
20. Garaycochea, I., Cid-Dresdener, H., Acta Cryst., 1961, 14, 200.
21. Weissenberg, K., Z. Physik, 1924, 23, 229.
22. Wiebenga, E.H., and Smits, D.W., Acta Cryst., 1950, 3, 265.
23. Smits, D.W., and Wiebenga, E.H., J. Sci. Instr., 1953, 30, 280.

24. Iball, J., J. Sci. Instr., 1954, 31, 71.
25. Lukesh, J.S., J. Chem. Phys., 1941, 9, 659.
26. Robertson, J.M., J. Sci. Instr., 1943, 20, 175.
27. Grenville-Wells, H.J., Acta Cryst., 1955, 8, 512.
28. Phillips, D.C., Acta Cryst., 1954, 7, 746.
29. Phillips, D.C., Acta Cryst., 1956, 9, 819.
30. Bullen, G.J., Acta Cryst., 1953, 6, 825.
31. Finney, A.J., Ph.D. Thesis, Tasmania, 1973.
32. Finney, A.J., J. Appl. Cryst., 1970, 3, 399.
33. Hamilton, W.C., Acta Cryst., 1965, 18, 502.
34. Cruickshank, D.W.J., and Robertson, A.P., Acta Cryst., 1953, 6, 698.
35. Acta Cryst., 1960, 13, 818-850.
36. Azaroff, L.V., and Buerger, M.J., "The Powder Method in X-Ray Crystallography", McGraw-Hill, New York, 1958.
37. Linderstrøm-Lang, K., Nature, Lond., 1937, 139, 713.
38. Zhdanov, G.S., and Zvonkova, Z.V., Ups. Khim., 1953, 22(1), 3.
39. Zvonkova, Z.V., Zh. fiz. khim., 1952, 26, 1798.
40. Zvonkova, Z.V., Zh. fiz. khim., 1953, 27, 98.
41. Zhdanov, G., Zvonkova, Z., and Glushkova, V., Zhurnal Fizichiskoi Khimii, 1953, 27, 106.
42. Hendricks, S.B., and Merwin, H.E., Am. Jour. Sci., 1928, 15, 34.
43. Maas, J., and Sand, J., Ber., 1909, 42, 2642.
44. Maas, J., and Sand, J., Ber., 1908, 41, 1500.
45. Pauling, L., "The Nature of the Chemical Bond", Oxford, 1960.
46. Lewis, J., Nyholm, R., and Smith, P.W., J.C.S., 1961, 4590.
47. Smith, P.W., Ph.D. Thesis, London, 1962.
48. Arland, S., Chatt, J., and Davies, N., Quart. Rev., 1958, 12, 265.
49. Zvonkova, Z.V., Zhurnal Fizichiskoi Khimii, 1957, 31, 2074.
50. Takeuchi, Y., and Saito, Y., Bull. Chem. Soc. Japan, 1957, 30, 319.
51. Takeuchi, Y., and Pepinsky, R., Z. für Krist., 1957, 109, 29.
52. Saito, Y., Takeuchi, Y., and Pepinski, R., Z. für Krist., 1955, 106, 476.
53. Pepinski, R., Z. für Krist., 1958, 110, 474.

54. Pearson, R.G., J. Am. Chem. Soc., 1963, 85, 3533.
55. Rosenheim, S., Ber., 1909, 42, 2295.
56. Ferrari, A., et al., Acta Cryst., 1965, 18, 367.
57. Nardelli, M., et al., Acta Cryst., 1966, 20, 349.
58. Turco, A., and Pecile, C., Nature, 1961, 191, 66.
59. Wheatley, P.J., Acta Cryst., 1969, 13, 80.
60. Knox, J.R., and Eriks, K., Inorg. Chem., ~~1968~~, 7, 84.
61. Podmore, L.P., Ph.D. Thesis, Tasmania, 1973.
62. Bellanca, A., Periodico Mineral (Rome), 1948, 17, 59.
63. Lindquist, I., Arkiv-Kemi, Mineral Geol., 1946, 24A, 1.
64. West, C.D. Z. Krist., 1935, 91A, 181.
65. Khodashova, T.S., Zh. Strukt. Khim., 1960, 1, 333.
66. Klug, H.P., Kummer, E., Alexander, L., J.A.C.S., 1948, 70, 3064.
67. Watanabe, T., and Atoji, M., ~~J.C.S. Jap~~, ^{J. Chem. Soc. Japan,} 1950, 71, 172.
68. Hopkins, T.E., Zalkin, A., Templeton, H., and Adamson, M.G.,
Inorg. Chem., 1966, 5, 1431.
69. Podmore, L.P., Smith, P.W., and Stoessiger, R.S., Chem. Comm., 1970, 221.
70. Podmore, L.P., and Smith, P.W., Aust. J. Chem., 1972, 25, 2521.
71. Stoessiger, R.S., Ph.D. Thesis, University of Tasmania, 1972.
72. Wells, A.F., "Structural Inorganic Chemistry", Clarendon, Oxford, 1962.
73. Edwards, A.J., J.C.S. Dalton, 1972, 1, 816.
74. Stähler, A., Ber. dt. chem. Ges., 1904, 37, 4411.
75. Ehrlich, P., and Seifert, H.J., Z. anorg. allg. Chem., 1959, 301, 282.
76. Crayton, P.H., and Thomson, W.A., J. inorg. nucl. Chem., 1963, 25, 742.
77. Horner, S.M., and Tyree, S.Y., Inorg. Chem., 1964, 3, 1173.
78. Seifert, H.J., and Loh, H.W., Inorg. Chem., 1966, 5, 1822.
79. Lequerica, M.C., Escalante, I., Noguerol, M., and Gutierrez de Celis, M.,
An. Quim., 1969, 55, 113.
80. Pajdowski, L., Roczn. Chem., 1969, 43, 2057.
81. Kilty, P.A., and Nicholls, D., J. chem. Soc., 1965, 4915.
82. Nicholls, D., and Wilkinson, D.N.J., J. chem. Soc., (A), 1969, 1232.

83. Lind, M.D., J. Chem. Phys., 1967, 47, 990.
84. Dance, I.G., and Freeman, H.C., Inorg. Chem., 1965, 4, 1555.
85. Morosin, B., Acta Cryst., 1966, 21, 280.
86. Marezio, M., Plettinger, H.A., and Zachariasen, W.H., Acta Cryst., 1961, 14, 234.
87. Mizuno, J., J. Phys. Soc. Japan., 1969, 15, 1412.
88. Mizuno, J., ibid., 1961, 16, 1574.
89. Andress, K.R., and Gundersman, J., Z. Krist., 1934, 87A, 345.
90. Fenn, R.H., Graham, A.J., Gillard, R.D., Nature 1967, 213, 1012.
91. Gillard, R.D., Laurie, S.H., and Mitchell, P.R., J.C.S., 1969, ~~2~~, 3006.
92. Greene, P.T., Orioli, P.L., J.C.S., 1969, 2, 1621.
93. Aleksandrov, G.C., Struchkov, Yu. T., Russ. Journ. Str. Chem., 1970, 11, 438.
94. Furlani, G., Tomlinson, A.A.G., Porta, P., Sgamellotti, A., J.C.S., 1970, ~~2~~, 2929.
95. Seifert, H.J., and Loh, H.W., Inorg. Chem., 1966, 5, 1822.
96. Nicholls, D., and Wilkinson, D.N., J. Chem. Soc. (A), 1969, 1232.
97. Gardner, H.J., Aust. J. Chem., 1967, 20, 2357.
98. Klemm, W., and Krose, E., Z. anorg. allgem. Chem., 1947, 253, 218.
99. Klemm, W., and Krose, E., Z. anorg. allgem. Chem., 1947, 253, 209.
100. Morosin, B., and Narath, J., J. Chem. Phys., 1964, 40, 1958.
101. Gregory, N.W., J. Am. Chem. Soc., 1951, 73, 472.
102. Wyckoff, R.W.G., "Crystal Structures" Vol. 3, Wiley, New York, 1964.
103. Colton, R., and Canterford, J.H., "Halides of the First Row Transition Metals", Wiley, London, 1969.
104. Nicholls, D., Coord. Chem. Rev., 1966, 1, 379.
105. Clark, R.J.H., "The Chemistry of Titanium and Vanadium", Elsevier, London, 1968.
106. Jack, K.H., and Gutmann, V., Acta Cryst., 1951, 4, 246.
107. McCarley, R.E., Roddy, J.W., and Berry, K.O., Inorg. Chem., 1964, 3, 50.
108. Chamberland, B.L. and Sleight, A.W., Solid State Commun., 1967, 5, 765.
109. Berry, K.O., Smardzewski, R.R. and McCarley, R.E., Inorg. Chem., 1969, 8, 1994.

110. Juza, D., Giegling, D. and Schäfer, H., Z. anorg. allgem. Chem., 1969, 366, 121.
111. Schafer, H., and Wartenpfuhl, F., J. Less-Common Metals, 1961, 3, 29.
112. McCarley, R.E., and Roddy, J.W., J. Inorg. Nucl. Chem., 1960, 15, 293.
113. Ehrlich, P., and Seifert, H.J., Z. anorg. allgem. Chem., 1959, 301, 282.
114. Babel, D., Pausenwang, G. and Viebahn, W., Z. Naturforsch., 1967, 22b, 1219.
115. Cretenet, J.C. and Cousseins, J.C., C.r. Séanc. Acad. Sci. Paris, 1968, 267c, 240.
116. Peacock, R.D., Progress in Inorganic Chemistry (Ed. F.A. Cotton), Interscience, New York, 1960. Vol. 2.
117. Bode, H. and Voss, E., Z. anorg. allgem. Chem., 1957, 290, 1.
118. Passerini, L. and Pirani, R., Gazz. Chim. Ital., 1932, 62, 279.
119. Cousseins, J.C. and Cretenet, J.C., C.r. Séanc. Acad. Sci. Paris, 1967, 265c, 1464.
120. Liebe, W., Weise, E. and Klemm, W., Z. anorg. allgem. Chem., 1961, 311, 281.
121. Babel, D., Z. Naturf., 1968, 23A, 1417.
122. Gladney, H.M., and Street, G.B., J. Inorg. Nucl. Chem., 1968, 30, 2949.
123. Wessel, G.J., and Ijdo, D.J., Acta Cryst., 1957, 10, 466.
124. Newnham, R.E., and Haan, Y.M. de, Z. Krist., 1962, 117, 235.

Appendix 1Computer Calculations

A major portion of the calculations involved in these structure determinations were made on an Elliott 503 digital computer, to which is linked a Digital Equipment Corporation PDP8/I computer. This linkage enables the Elliott 503 to make use of the DEC tape and disk file units of the PDP8/I and enhances its own main store capacity of 8192 (8K) words and core-backing-store capacity of 16384 (16K) words. The basic language is ALGOL with extensive use being made of machine-coded procedure inserts. The suite of X-ray crystallographic programs was designed and written by Finney of this department over the past four years and is at present incomplete^{31,32}.

A.1.1. Description of Program Suite

The completed suite envisages the use of thirteen programs, which includes provision for Direct Methods calculations. In this work, however, only six of these programs were used and these are shown in Fig. 1.

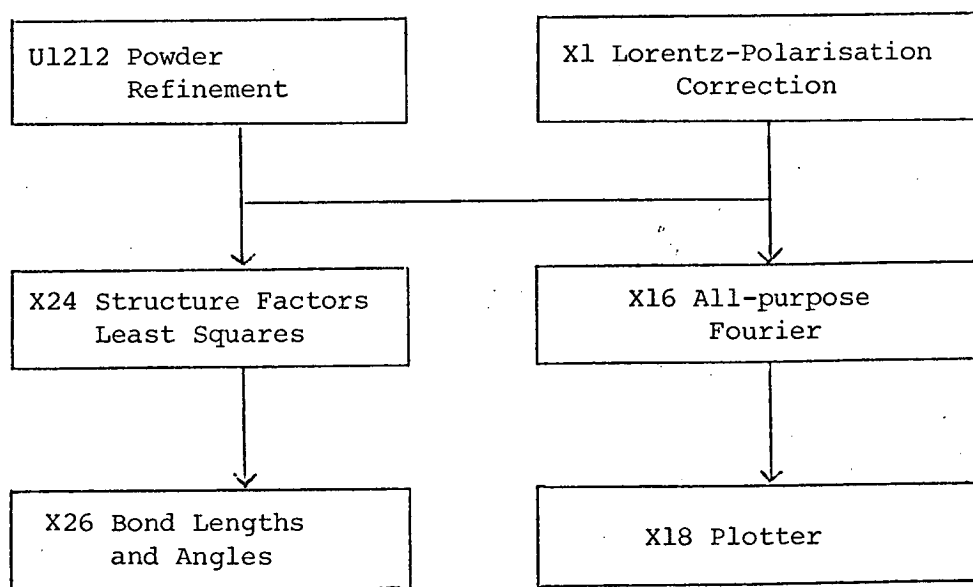


Fig. 1. Program Suite

A.1.2. The Lorentz-Polarisation Correction Program (X1)

In using observed intensity data for structure determination use is made of the structure amplitude $|F|$ where:

$$|F| \propto \sqrt{I} \quad [I = \text{intensity}]$$

These structure amplitudes are required for calculating electron density maps used during structure determinations. This program (X1) converts the raw intensities to $|F_{\text{observed}}|$ by using the following expression:

$$|F_{(hkl)}| = \frac{\sqrt{I_{(hkl)}}}{L_p}$$

The Lorentz factor, L , is required to allow for the specific type of motion of the crystal in the Weissenberg camera geometry used in this study and is given by:

$$L = \frac{\sin\theta}{\sin 2\theta (\sin^2\theta - \sin^2\mu)^{1/2}} \quad (\theta = \text{Bragg angle})$$

$$\mu = \text{equi-inclination setting})$$

The polarisation factor, p , is given by

$$p = \frac{1 + \cos^2 2\theta}{2}$$

and arises from polarisation of the X-ray beam on reflection by a crystal. It is a simple function of 2θ and is independent of the type of data collection technique. The program accepts unit cell constants, wavelength of radiation used, equi-inclination angle for the first level, rotation axis and scaled intensity data and generates a set of $|F_{hkl}| \times 10^2$, each plane having been corrected for Lorentz and polarisation effects.

A.1.3. The Fourier Program (X16)

This program is used for calculating Fourier syntheses of the following types:

- (a) Patterson
- (b) Electron density
- (c) Difference Fourier
- (d) E-maps (Direct Methods)

The expression required for electron density maps is of the form:

$$\rho_{(xyz)} = \frac{1}{V} \sum_{h,k,\ell} \sum_{h,k,\ell = -\infty}^{+\infty} F_{(hkl)} e^{-2\pi i(hx + ky + \ell z)}$$

and in this program the equation is rewritten as:

$$\rho_{(xyz)} = \frac{2}{V} \sum_{h,k,\ell} [A_{(hkl)} \cos 2\pi(hx + ky + \ell z) + B_{(hkl)} \sin 2\pi(hx + ky + \ell z)]$$

where $F_{(hkl)} = A_{(hkl)} + iB_{(hkl)}$,

and rearranged to read:

$$\rho_{(xyz)} = \frac{2}{V} \left[\begin{array}{ccc} \infty & \infty & \infty \\ \sum & \sum & \sum \\ h & k & l \end{array} A_{(hkl)} \quad (\text{ccc-css-scs-ssc}) \right. \\ \left. + \begin{array}{ccc} \infty & \infty & \infty \\ \sum & \sum & \sum \\ h & k & l \end{array} B_{(hkl)} \quad (\text{ccs} + \text{csc} + \text{scc} - \text{sss}) \right]$$

(where e.g., $\text{csc} = \cos 2\pi h x \sin 2\pi k y \cos 2\pi l z$ etc.)

Since the compounds discussed in this work all crystallized in centrosymmetric space groups the expression can be further simplified to delete the B term, and in some cases further product terms drop out for specified index parity groups. For example, in the case of $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$ which crystallizes in the monoclinic space group C2/m the expression calculated for the electron density was:

$$\rho_{(xyz)} = \frac{2}{V} \sum_{h,k,l}^{\infty} A_{(hkl)} \quad (\text{ccc} + \text{scs})$$

The program (X16) operates in several steps:

- a) Sorts the data for more efficient calculation;
- b) Corrects the reflections for multiplicity;
- c) Attaches a code word to each reflection to control the form of the trigonometric function to be used;
- d) Calculates sections of the electron density function and displays these on a lineprinter;
- e) Stores these sections for subsequent plotting by program X(18).

$$F_{(hkl)} = \sum_{j=1}^p n_j f_j \sum_{s=1}^p \exp(-h^T B_{js} h) \cos 2\pi h^T x_{js} \\ + i \sum_{j=1}^n n_j f_j \sum_{s=1}^p \exp(-h^T B_{js} h) \sin 2\pi h^T x_{js}$$

where n_j is the occupancy parameter of the j^{th} atom, f_j is the scattering power of $\sin\theta_{(hkl)}/\lambda$ of the j^{th} atom, B_{js} is a 3×3 temperature factor matrix for the j^{th} atom in symmetry position s , x_{js} is the coordinate vector of the j^{th} atom in position s ,

x_{js} is the coordinate vector of the j^{th} atom in position s ,

h is the reciprocal space vector \underline{h} , \underline{k} , \underline{l} and h^T its transpose,

n is the number of independent atoms,

p is the number of symmetry positions.

The presence of symmetry elements simplifies the expression for $F_{(hkl)}$ and these modified forms of the structure factors are given in the appropriate chapters where necessary.

The program outputs the calculations on a lineprinter and stores the information in the core-backing-store for use in subsequent Fourier computations.

The second stage in this program allows for the refinement of structural parameters by the least squares method. This involves the full-matrix least squares refinement generating corrections for the atomic parameters. The course of the refinement may be followed by the calculation of a residual factor:

$$R = \sum \left[\left| F_o \right| - \left| F_c \right| / \left| F_o \right| \right]$$

The output from this part of the program can be used in a cyclic manner as input for another round of structure factor calculations and parameter refinement.

A.1.4. The Plotter Program (X18)

The lineprinter output of the Fourier program only gives sections of rectangular cell geometry and these only approximately to scale. The plotter program overcomes this deficiency as it can be used to plot contoured sections of all cell types to a high degree of accuracy. An example of one of these plots is shown as Fig. 2. Fourier Plot.

A.1.5. The Structure Factors-Least Squares Program (X24)

The structure factor $F_{(hkl)}$ is a function of \underline{h} , \underline{k} , and $\underline{\ell}$, the Miller index of a reflection from a lattice plane. Its modulus is called the structure amplitude, and is defined as the amplitude of the radiation scattered in the order \underline{h} , \underline{k} , $\underline{\ell}$ by the contents of one unit cell, to that scattered by a single electron under the same conditions. The generalised structure factor can be written as:

$$F = \sum_j f_j e^{-i\delta_j} \quad \left[\begin{array}{l} f_j \text{ scattering factor of the} \\ j^{\text{th}} \text{ atom} \\ \delta_j \text{ phase with respect to an origin.} \end{array} \right]$$

and for a given reflection \underline{h} , \underline{k} , $\underline{\ell}$ as:

$$F_{(hkl)} = \sum_j f_j e^{-2\pi i(hx_j + ky_j + \ell z_j)}$$

[x_j , y_j , z_j are the fractional
coordinates of the j^{th} atom]

When using the structure factor program for calculating the structure factor $F_{(hkl)}$, for each reflection based on parameters specified for a trial or final structural model the expression used is:

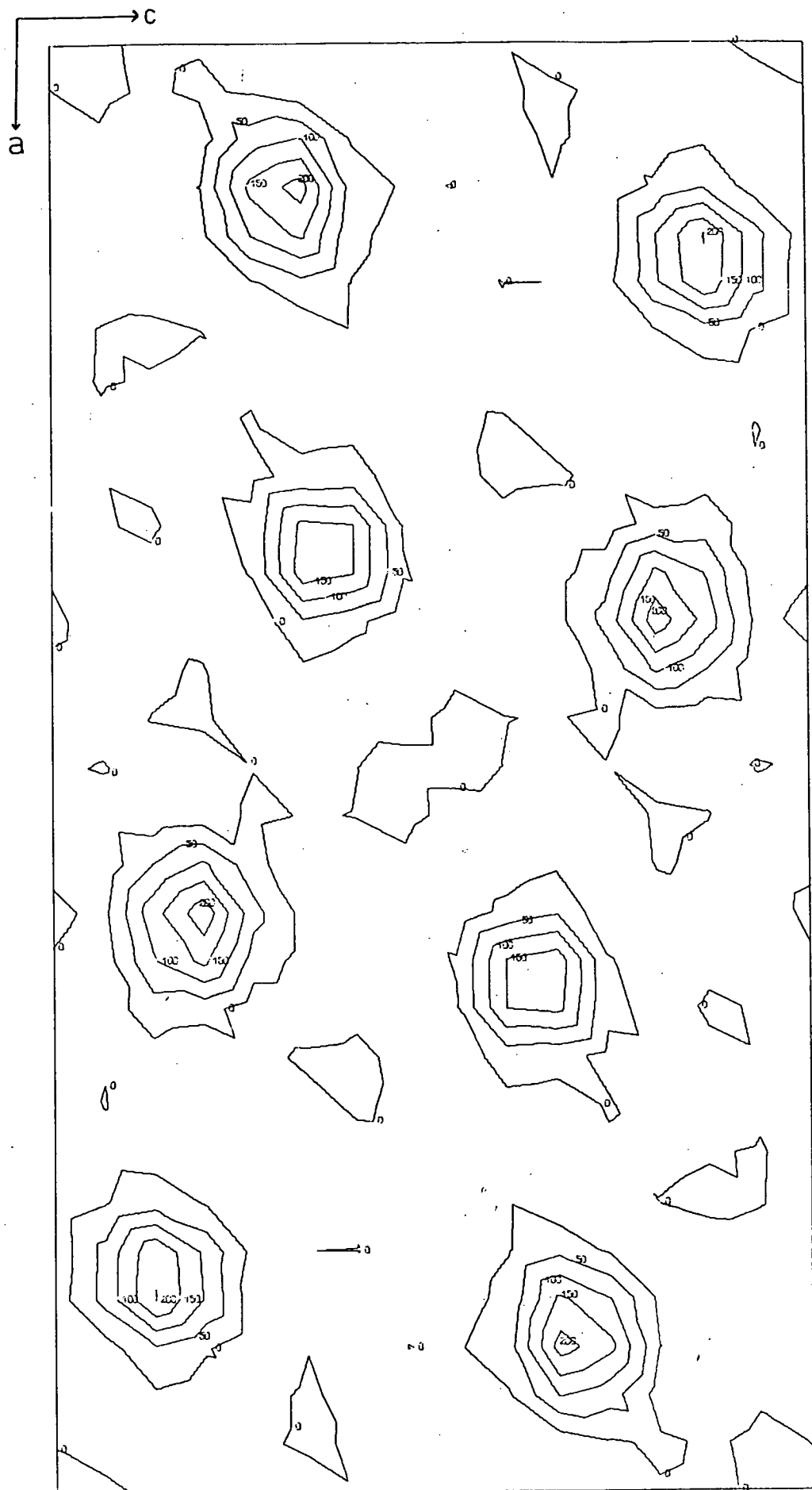


FIG. 2

Fourier Section $y = 0$, for $K_2(MoCl_5H_2O)$

Sample Plotter Output

(Contour interval = 50.0)

Alternatively it can generate data for use in further Fourier calculations or provide the input data by way of the core-backing store for calculations of bond lengths and bond angles and the provision of final detailed lists of calculated and observed structure factors.

A sample list of input and output data from a structure factor-least squares calculation on $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br} \cdot 2\text{H}_2\text{O}$ is shown as Table A.1.1.

A.1.6. The Bond-Lengths and Bond-Angles Program (X26)

Of major interest in the determination of these crystal structures is that it makes possible the derivation of structural parameters other than the gross molecular structure of the compounds under study. Two of the main parameters which can be derived are bond-lengths and bond-angles. This program (X26) accepts as input refined coordinate parameters and unit cell data from the Structure Factors/Least Squares program and outputs a list of bond-lengths and bond-angles together with standard deviations in these parameters.

The fundamental equation for the distance between two points in a generalised triclinic lattice is of the form:

$$\begin{aligned} \ell = \sqrt{(\Delta x a)^2 + (\Delta y b)^2 + (\Delta z c)^2 + 2ab \Delta x \Delta y \cos \gamma} \\ + 2ac \Delta x \Delta z \cos \beta + 2bc \Delta y \Delta z \cos \alpha \end{aligned}$$

where the two points have fractional coordinates (x_1, y_1, z_1) and (x_2, y_2, z_2) and $a, b, c, \alpha, \beta, \gamma$ are the unit cell parameters.

This equation of course can be simplified for lattices of higher symmetry.

In the case of bond angles between any three points A, B and C it is possible to calculate the angle θ by the equation:

$$\theta = \cos^{-1} \left[\frac{(AB)^2 + (AC)^2 - (BC)^2}{2 (AB) (AC)} \right]$$

STRUCTURE FACTORS-LEAST SQUARES INPUT-OUTPUT DATA

[VBr₂(H₂O)₄]Br₂H₂O

NUMBER OF CYCLES	3
NUMBER OF VARIABLES	22
NUMBER OF OBSERVATIONS	362
NUMBER OF F-CURVES	3
NUMBER OF ATOMS	6
NUMBER OF SYMMETRY POSITIONS	2
NUMBER OF SCALES	4
NUMBER OF ISOTROPIC ATOMS	6

AXIS OF DATA COLLECTION	H
LOWEST INDEX IS	0
OBSERVATIONS ARE	F
WEIGHTING	SET = 1.0
CENTROSYMMETRIC	YES

SCATTERING CURVES:

VARIATION OF						
22.100	21.710	20.640	19.120	17.470	15.790	14.210
12.750	11.560	10.520	9.6700	9.0400	8.4100	7.9900
7.4700	7.2700	6.9700	6.7300	6.4900	6.2700	6.0500
5.8400	5.6200	5.4100	5.2000	5.0000	4.7900	4.5900
4.3900	4.2000	4.0100	3.8200			
BROMINE -						
35.100	34.160	31.910	29.230	26.750	24.640	22.860
21.320	19.920	18.640	17.370	16.090	14.910	13.840
12.770	11.840	10.920	10.160	9.4000	8.7900	8.1800
7.7100	7.2400	6.8700	6.5000	6.2200	5.9500	5.7200
5.5000	5.3300	5.1600	4.9900			
OXYGEN 2-						
8.0000	7.7960	7.2560	6.4870	5.6330	4.8110	4.0900
3.4940	3.0160	2.6370	2.3400	2.1100	1.9370	1.8090
1.7190	1.6560	1.6150	1.5860	1.5720	1.5620	1.5570
1.5530	1.5520	1.5510	1.5500	1.5500	1.5500	1.5500
1.5500	1.5500	1.5500	1.5500			

SYMMETRY POSITIONS:

X.	Y.	Z.
-X.	Y+1/2.	-Z+1/2.

RECIPROCAL CELL DATA:

A* = .15700 B* = .15267 C* = .08179 COS(ALPHA*) = .00000 COS(BETA*) = .10713 COS(GAMMA*) = .00000

DATA SCALES:

3.9800*
4.3000*
4.3400*
4.9200*

OVERALL T/FACOR: .00000
ATOMIC PARAMETERS BEFORE REFINEMENT:

V	FCURVE	1
	OCCUPANCY	1.0000
	X	.00000000
	Y	.00000000
	Z	.00000000
	B	1.7660*
BR 1	FCURVE	2
	OCCUPANCY	1.0000
	X	.50000000
	Y	.00000000
	Z	.50000000
	B	2.6000*
BR 2	FCURVE	2
	OCCUPANCY	2.0000
	X	.28200000*
	Y	-.02300000*
	Z	.16100000*
	B	2.7900*
H2O 1	FCURVE	3
	OCCUPANCY	2.0000
	X	.79900000*
	Y	-.01400000*
	Z	.29900000*
	B	1.7700*
H2O 2	FCURVE	3
	OCCUPANCY	2.0000
	X	.20000000*
	Y	.12700000*
	Z	-.06900000*
	B	3.0000*
H2O 3	FCURVE	3
	OCCUPANCY	2.0000
	X	-.07600000*
	Y	.26300000*
	Z	.06300000*
	B	3.0000*

TABLE A.1d(CONT.)

STRUCTURE FACTORS-LEAST SQUARES INPUT-OUTPUT DATA

AGREEMENT FACTORS BASED ON PARAMETERS PRIOR TO REFINEMENT									
SIGMA(FU)									
718136									
45.3263									
FACTORS: NUMERATOR									
DENOMINATOR									
F-FACTOR									
WITH UNRES									
13090.4									
117228									
11.1666									
OBS ONLY									
13070.4									
117228									
11.1666									
WITH UNRES (K)									
647.429									
7566.70									
11.1995									
OBS ONLY (M)									
647.429									
7566.70									
11.1995									

FACTORS: NUMERATOR									
DENOMINATOR									
F-FACTOR									
WITH UNRES									
13090.4									
117228									
11.1666									
OBS ONLY									
13070.4									
117228									
11.1666									
WITH UNRES (K)									
647.429									
7566.70									
11.1995									
OBS ONLY (M)									
647.429									
7566.70									
11.1995									

FACTORS: NUMERATOR									
DENOMINATOR									
F-FACTOR									
WITH UNRES									
13090.4									
117228									
11.1666									
OBS ONLY									
13070.4									
117228									
11.1666									
WITH UNRES (K)									
647.429									
7566.70									
11.1995									
OBS ONLY (M)									
647.429									
7566.70									
11.1995									

FACTORS: NUMERATOR									
DENOMINATOR									
F-FACTOR									
WITH UNRES									
13090.4									
117228									
11.1666									
OBS ONLY									
13070.4									
117228									
11.1666									
WITH UNRES (K)									
647.429									
7566.70									
11.1995									
OBS ONLY (M)									
647.429									
7566.70									
11.1995									

FACTORS: NUMERATOR									
DENOMINATOR									
F-FACTOR									
WITH UNRES									
13090.4									
117228									
11.1666									
OBS ONLY									
13070.4									
117228									
11.1666									
WITH UNRES (K)									
647.429									
7566.70									
11.1995									
OBS ONLY (M)									
647.429									
7566.70									
11.1995									

FACTORS: NUMERATOR									
DENOMINATOR									
F-FACTOR									
WITH UNRES									
13090.4									
117228									
11.1666									
OBS ONLY									
13070.4									
117228									
11.1666									
WITH UNRES (K)									
647.429									
7566.70									
11.1995									
OBS ONLY (M)									
647.429									
7566.70									
11.1995									

FACTORS: NUMERATOR									
DENOMINATOR									
F-FACTOR									
WITH UNRES									
13090.4									
117228									
11.1666									
OBS ONLY									
13070.4									
117228									
11.1666									
WITH UNRES (K)									
647.429									
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TABLE A.1.1(CONT.)

STRUCTURE FACTORS-LEAST SQUARES INPUT-OUTPUT DATA

$$\frac{[VBr_2(H_2O)]Br_2 \cdot 2H_2O}{2}$$

AGREEMENT FACTORS BASED ON PARAMETERS PRIOR TO REFINEMENT

SIGMA(A*Δ)				702463
STANDARD DEV.				45.4547
R-FACTORS: NUMERATOR				
WITH UNOBS				
OBS ONLY				
WITH UNOBS (Δ)				
OBS ONLY (Δ)				
R-FACTORS: DENOMINATOR				
WITH UNOBS				
OBS ONLY				
WITH UNOBS (M)				
OBS ONLY (M)				

R-FACTOR ANALYSIS (AS A FUNCTION OF SIN(TH)/L)

RANGE					R-FACTOR				
SIGMA(F0)					SIGMA(Δ)				
.000000	.050000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.050000	.100000	.396.000	23.4197	5.91406	.000000	.000000	.000000	.000000	.000000
.100000	.150000	2649.00	238.522	8.99666	.000000	.000000	.000000	.000000	.000000
.150000	.200000	9828.00	982.043	9.99230	.000000	.000000	.000000	.000000	.000000
.200000	.250000	12789.0	1028.31	8.04059	.000000	.000000	.000000	.000000	.000000
.250000	.300000	13484.0	1595.89	11.8355	.000000	.000000	.000000	.000000	.000000
.300000	.350000	14114.0	1497.57	10.6105	.000000	.000000	.000000	.000000	.000000
.350000	.400000	15678.0	1658.48	10.5784	.000000	.000000	.000000	.000000	.000000
.400000	.450000	13061.0	1366.72	10.4641	.000000	.000000	.000000	.000000	.000000
.450000	.500000	12531.0	1293.49	10.3223	.000000	.000000	.000000	.000000	.000000
.500000	.550000	9514.00	1234.32	12.9737	.000000	.000000	.000000	.000000	.000000
.550000	.600000	7284.00	999.081	13.7161	.000000	.000000	.000000	.000000	.000000
.600000	.650000	5900.00	1110.85	18.8280	.000000	.000000	.000000	.000000	.000000
.650000	.700000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.700000	.750000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.750000	.800000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.800000	.850000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.850000	.900000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
.900000	.950000	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000

R-FACTOR ANALYSIS (BY LEVELS)

LEVEL	SIGMA(F0)	SIGMA(Δ)	R-FACTOR	N
0	26984.0	3032.34	11.2375	76
1	33148.0	3418.90	10.3140	97
2	30267.0	3314.65	10.9514	97
3	26829.0	3262.62	12.1608	93

Fig. 3 showing the appropriate lengths.

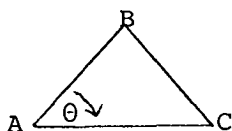


Fig. 3

Bond Angles

The program outputs a list of appropriate bond-lengths and bond-angles together with standard deviations in all parameters.

A.1.7. Powder Refinement Program (UL212)

In order to obtain accurate cell dimensions X-ray powder diffraction data were collected for all compounds using either KCl or silicon metal as internal standards. Initial cell dimensions were obtained from single crystal Weissenberg photographs and these were refined by the least squares method using this program.

The input to the program basically consists of a set of trial cell dimensions and a list of observed $\sin^2\theta$ values. The unit-cell parameters are refined by solving the overdetermined system of linear equations obtained by indexing the powder pattern.

A sample output of data from this program is shown as Table A.1.2.

TABLE A.1.2

SAMPLE DATA OUTPUT FROM PROGRAM U1212

FOR $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$

THE DATA TO BE REFINED, CSVCL WFO 3
 CONSISTS OF 20 SINE SQUARED THETA VALUES COLLECTED AT A WAVELENGTH OF 1.54050 ANGSTROM UNITS
 THE INDEX RANGE EXTENDS UP TO $h = 6$, $k = 12$, $l = 6$ AND THE INDEXING IS REQUIRED
 WITH AN INITIAL ACCURACY OF .001666 IN θ -VALUE UNITS.
 THE ASSUMED SYMMETRY IS MONOCLINIC WITH h -AXIS UNIQUE
 THE TRIAL CELL IS:
 CELL ELEMENTS:

A= 17.9200 B= 6.1600 C= 7.1050 ALPHA= 90.0000 BETA= 107.0000 GAMMA= 90.0000

THE INPUT DATA AS θ -VALUES

		1		.013619	
		2		.021659	
		3		.025637	
		4		.046453	
		5		.054763	
		6		.056870	
		7		.064269	
		8		.081849	
		9		.087631	
		10		.093665	
		11		.096379	
		12		.104385	
		13		.112088	
		14		.115493	
		15		.118409	
		16		.120903	
		17		.124106	
		18		.126971	
		19		.130494	
		20		.150653	
OBS	H	K	L	OCALC	DIFF
.013619	2	0	0	.013620	.000001
.021659	0	0	1	.021661	.000002
	0	0	-1	.021661	.000002
.025637	2	0	-1	.025238	.000399
.046453	2	0	1	.045325	.001128
	1	1	-1	.046398	.000055
.054763	4	0	0	.054482	.000281
	4	0	-1	.056055	.001292
	1	1	1	.056442	.001679
.056870	4	0	-1	.056055	.000815
	1	1	1	.056442	.000428
	3	1	0	.057000	.000130
.064269	3	1	-1	.063595	.000675
.081849	2	0	-2	.080177	.001672
.087631	0	0	2	.086644	.000987
	0	0	-2	.086644	.000987
.093665	3	1	1	.093726	.000061
.096379	4	0	1	.096231	.000148
.104385	0	2	0	.105414	.001029
.112088	5	1	0	.111481	.000606
	3	1	-2	.113512	.001424
.115493	6	0	-1	.114113	.001379
.118409	2	2	0	.119035	.000626
.120903	2	0	2	.120352	.000551
	6	0	0	.122584	.001681
.124106	6	0	0	.122584	.001522
.126971	1	1	2	.126447	.000524
	0	2	-1	.127075	.000104
	0	2	1	.127075	.000104
.130494	2	2	-1	.130652	.000158
.150653	2	2	1	.150739	.000087
MEAN= .000524				STANDARD DEVIATION= .000526 FOR 20 INDEXED LINES	

CELL ELEMENTS:

A= 17.8035 B= 6.1763 C= 7.0542 ALPHA= 90.0000 BETA= 106.6126 GAMMA= 90.0000

MEAN= .000209 STANDARD DEVIATION= .000121 FOR 20 INDEXED LINES

CELL ELEMENTS:

A= 17.8027 B= 6.1779 C= 7.0570 ALPHA= 90.0000 BETA= 106.6258 GAMMA= 90.0000

MEAN= .000201 STANDARD DEVIATION= .000129 FOR 20 INDEXED LINES

CELL ELEMENTS:

A= 17.8027 B= 6.1779 C= 7.0570 ALPHA= 90.0000 BETA= 106.6258 GAMMA= 90.0000

MEAN= .000201 STANDARD DEVIATION= .000129 FOR 20 INDEXED LINES

NO IMPROVEMENT

H	K	L	OBS	OCALC	Δ	DEWOLFF
2	0	0	.013619	.013746	.000127	.002165
0	0	1	.021659	.021870	.000211	.001876
2	0	-1	.025637	.025644	.000058	.001775
1	1	-1	.046453	.046547	.000094	.001444
4	0	0	.054763	.054985	.000222	.001359
4	0	-1	.056870	.057011	.000141	.001340
3	1	-1	.064269	.064117	.000152	.001280
2	0	-2	.081849	.081363	.000486	.001166
0	0	2	.087631	.087481	.000150	.001135
3	1	1	.093665	.093883	.000218	.001106
4	0	1	.096379	.096699	.000320	.001094
0	2	0	.104385	.104805	.000420	.001059
5	1	0	.112088	.112115	.000027	.001030
6	0	-1	.115493	.115820	.000327	.001017
2	2	0	.118409	.118551	.000143	.001007
2	0	2	.120903	.121071	.000168	.000999
6	0	0	.124106	.123716	.000390	.000988
1	1	2	.126971	.127040	.000069	.000979
2	2	-1	.130494	.130459	.000035	.000968
2	2	1	.150653	.150343	.000310	.000912

Appendix 2Density Determination

To facilitate crystal structure determination it is necessary to calculate the number of molecules of a compound that occupy the unit cell. For this purpose density measurements on the compounds are required.

In some cases the densities have been determined by other workers and where these showed reasonable agreement with calculated values only an approximate check was made on the densities of the crystals concerned. This consisted of finding a liquid of slightly less density than the crystalline material and in which it was insoluble and observing that small crystals did just sink in the medium.

Where original determinations had to be made, the gradient tube method was used^{11,37}. In all cases some idea of the density expected was known. Two miscible liquids covering the density range were mixed in a vertical tube with a plunger-type stirrer, giving linear density gradient near the surface.

The gradient was calibrated using drops of immiscible liquids of known density. Small crystals of the samples were then introduced into the column and their densities measured from the point at which they became stationary. This method proved adequate for the use that was made of the densities and such problems as cavities or inclusions in the crystalline samples could be ignored.

Appendix 3

Structure Factor Tables

The following fourteen tables comprise lists of structure factors, observed and calculated, for each of the structures reported in this thesis. The data in Tables A3.1 and A3.3 were extracted from output of the structure factors program discussed in Section 2.2. Table A3.2 contains only observed structure factors for the weak layer line data collected for $K_3[Cr(NCS)_6] \cdot 4H_2O$ (see also Section 2.2). The data in Tables A3.4 to A3.14 have been obtained directly as output from the ALGOL computer program X24 (Appendix 1).

TABLE A3.1

F(OBS), F(CALC) FOR K₃[Cr(CNS)₆]·4H₂O

H.	K	L	K*FOBS	F(CALC)	1	1	2	313.00	235.18	U	6	4	446.00	547.93
0	2	0	116.00	61.87	1	2	2	427.00	241.80	0	7	4	205.00	65.16
0	3	0	256.00	390.13	1	3	2	171.00	39.66	0	8	4	256.00	172.90
0	4	0	185.00	33.76	1	4	2	303.00	262.37	0	12	4	209.00	179.27
0	5	0	223.00	168.21	1	5	2	309.00	173.57	1	0	4	80.00	15.29
0	6	0	850.00	920.22	1	7	2	200.00	244.43	1	1	4	293.00	417.58
0	8	0	213.00	191.06	2	10	2	218.00	190.00	1	3	4	336.00	218.10
0	12	0	376.00	376.28	2	0	2	170.00	208.63	1	4	4	140.00	188.49
1	2	0	109.00	38.02	2	1	2	222.00	130.30	1	5	4	328.00	262.73
1	3	0	155.00	40.19	2	2	2	709.00	803.79	1	6	4	249.00	146.43
1	4	0	466.00	264.01	2	3	2	191.00	54.01	1	7	4	135.00	75.70
1	5	0	155.00	68.70	2	5	2	407.00	280.43	2	1	4	222.00	217.78
1	6	0	224.00	73.02	2	6	2	122.00	90.85	2	2	4	291.00	332.75
1	7	0	228.00	45.22	3	8	2	258.00	294.33	2	3	4	96.00	24.05
2	0	0	116.00	61.87	3	0	2	669.00	922.24	2	4	4	108.00	109.56
2	1	0	109.00	38.02	3	1	2	304.00	193.36	2	6	4	151.00	28.63
2	2	0	741.00	972.97	3	2	2	212.00	122.12	2	8	4	369.00	323.50
2	3	0	123.00	74.03	3	3	2	525.00	507.84	3	0	4	379.00	335.72
2	4	0	176.00	113.13	3	4	2	255.00	27.54	3	1	4	217.00	186.01
2	8	0	709.00	648.21	3	5	2	169.00	186.05	3	2	4	367.00	285.17
3	0	0	256.00	390.13	3	6	2	460.00	360.01	3	3	4	170.00	103.77
3	1	0	153.00	40.19	3	7	2	200.00	27.16	3	5	4	182.00	231.64
3	2	0	123.00	74.03	3	8	2	248.00	187.92	3	8	4	277.00	248.25
3	3	0	528.00	493.41	3	9	2	247.00	142.70	4	0	4	332.00	116.53
3	4	0	124.00	27.22	4	0	2	406.00	310.79	4	1	4	157.00	139.18
3	5	0	168.00	144.06	4	1	2	217.00	158.78	4	2	4	108.00	130.64
3	6	0	184.00	85.33	4	3	2	109.00	87.65	4	3	4	118.00	147.80
4	0	0	185.00	33.76	4	4	2	450.00	421.65	4	4	4	230.00	255.70
4	1	0	466.00	264.01	4	5	2	262.00	178.35	4	6	4	147.00	74.06
4	2	0	176.00	113.13	4	6	2	197.00	111.77	4	8	4	155.00	157.49
4	3	0	124.00	27.22	5	0	2	240.00	270.66	5	0	4	255.00	144.54
4	4	0	914.00	918.04	5	2	2	454.00	241.26	5	1	4	270.00	195.90
4	5	0	208.00	109.41	5	3	2	288.00	189.02	6	0	4	618.00	612.82
5	0	0	223.00	168.21	5	5	2	407.00	303.50	6	1	4	152.00	56.04
5	1	0	155.00	68.70	5	6	2	148.00	27.06	6	4	4	181.00	89.19
5	3	0	168.00	144.06	6	0	2	319.00	242.93	7	0	4	359.00	281.30
5	4	0	208.00	109.41	6	1	2	181.00	95.71	7	2	4	175.00	197.71
5	5	0	272.00	183.20	6	2	2	307.00	179.67	7	3	4	235.00	188.95
5	6	0	171.00	52.73	6	3	2	430.00	319.42	8	2	4	334.00	308.58
6	0	0	850.00	920.22	6	5	2	209.00	104.42	9	1	4	153.00	121.50
6	1	0	224.00	73.02	6	6	2	296.00	354.00	9	2	4	219.00	110.67
6	3	0	184.00	85.33	7	0	2	233.00	135.10	12	0	4	229.00	160.73
6	5	0	171.00	52.73	7	1	2	361.00	253.32	0	1	5	70.00	29.16
6	6	0	693.00	618.81	7	2	2	358.00	111.83	0	2	5	164.00	190.16
7	1	0	228.00	45.22	7	3	2	224.00	145.54	0	3	5	135.00	155.87
8	0	0	213.00	191.06	7	4	2	148.00	225.79	0	4	5	188.00	244.36
8	2	0	709.00	648.21	7	5	2	115.00	76.54	0	5	5	224.00	198.26
12	0	0	376.00	376.28	8	0	2	281.00	272.71	0	10	5	293.00	45.03
0	2	1	198.00	91.00	9	2	2	247.00	187.04	1	2	5	168.00	108.08
0	3	1	387.00	426.84	9	3	2	209.00	174.25	1	3	5	157.00	50.20
0	4	1	443.00	321.45	9	4	2	338.00	166.32	1	5	5	208.00	174.31
0	5	1	464.00	354.13	10	1	2	257.00	36.68	1	8	5	241.00	159.25
0	6	1	181.00	40.27	10	2	2	335.00	222.42	2	3	5	278.00	293.09
0	7	1	123.00	83.16	11	2	2	257.00	139.43	2	4	5	301.00	318.44
0	8	1	257.00	183.52	11	2	2	266.00	202.80	3	0	5	101.00	105.46
1	1	1	203.00	324.66	0	1	3	295.00	307.66	3	1	5	129.00	119.63
1	2	1	290.00	383.08	0	2	3	574.00	700.91	3	4	5	229.00	18.28
1	3	1	207.00	236.88	0	3	3	512.00	510.07	3	5	5	163.00	208.61
1	4	1	280.00	348.89	0	4	3	185.00	77.96	4	0	5	412.00	487.01
1	5	1	257.00	263.20	0	5	3	220.00	130.28	4	4	5	133.00	66.62
1	7	1	206.00	98.49	0	6	3	303.00	21.72	4	7	5	192.00	13.20
1	8	1	266.00	209.06	0	7	3	485.00	519.90	5	0	5	414.00	322.50
2	0	1	320.00	392.87	0	8	3	225.00	185.14	5	3	5	211.00	190.94
2	1	1	281.00	183.68	1	0	3	208.00	191.02	5	7	5	186.00	32.01
2	2	1	125.00	150.93	1	2	3	131.00	285.56	6	0	5	122.00	183.57
2	3	1	372.00	561.00	1	3	3	209.00	354.02	6	2	5	215.00	191.92
2	4	1	161.00	181.11	1	4	3	272.00	209.50	12	0	5	220.00	52.56
2	5	1	193.00	126.33	1	5	3	371.00	296.99					
2	6	1	278.00	245.86	2	6	3	273.00	277.13					
3	0	1	463.00	428.62	2	7	3	214.00	22.62					
3	1	1	81.00	84.24	2	8	3	584.00	785.53					
3	2	1	413.00	382.13	2	9	3	272.00	100.56					
3	3	1	100.00	85.98	2	10	3	466.00	283.96					
3	4	1	177.00	83.76	2	11	3	282.00	241.77					
3	5	1	328.00	368.40	2	12	3	146.00	13.17					
3	6	1	166.00	195.00	2	13	3	568.00	596.09					
4	0	1	375.00	469.24	3	14	3	143.00	115.44					
4	1	1	114.00	7.12	3	15	3	153.00	79.98					
4	2	1	102.00	8.10	3	16	3	77.00	194.08					
4	4	1	150.00	230.85	3	17	3	218.00	0.71					
4	5	1	226.00	279.09	3	18	3	200.00	161.94					
4	6	1	237.00	157.75	3	19	3	150.00	71.96					
5	0	1	576.00	440.57	4	20	3	336.00	226.46					
5	1	1	187.00	127.38	4	21	3	261.00	65.91					
5	2	1	140.00	6.46	4	22	3	468.00	316.30					
5	3	1	385.00	526.57	4	23	3	332.00	301.55					
5	4	1	219.00	131.25	4	24	3	276.00	277.51					
5	6	1	463.00	378.87	4	25	3	128.00	109.44					
6	0	1	175.00	56.82	5	26	3	196.00	50.75					
6	1	1	186.00	24.35	5	27	3	245.00	157.04					
6	2	1	126.00	115.36	5	28	3	494.00	495.59					
6	3	1	166.00	21.08	6	29	3	346.00	288.49					
6	5	1	243.00	251.98	6	30	3	276.00	100.14					
7	0	1	123.00	189.90	6	31	3	164.00	87.02					
7	1	1	184.00	139.39	6	32	3	123.00	11.79					
7	2	1	170.00	96.36	6	33	3	454.00	470.58					
7	3	1	180.00	33.97	7	34	3	140.00	19.07					
8	0	1	397.00	299.64	7	35	3	245.00	195.74					
8	1	1	201.00	109.01	7	36	3	143.00	35.72					
8	2	1	149.00	19.86	8	37	3	157.00	74.83					
8	3	1	278.00	287.36	8	38	3	602.00	556.08					
9	0	1	294.00	158.17	8	39	3	407.00	226.78					
9	3	1	162.00	114.80	10	40	3	229.00	220.00					
10	1	1	228.00	125.25	10	41	3	267.00	284.67					
11	0													

TABLE A3.2

F(OBS), F(CALC) FOR K_3 (MO(CNS))₆ · 4H₂O

0	3	0	90.16	146.51	2	6	1	79.41	59.45	2	6	2	70.50	65.61	2	1	5	65.50	43.94
0	4	0	43.30	3.66	2	7	1	47.56	14.20	2	7	2	40.18	23.54	2	2	5	50.28	15.35
0	5	0	43.70	81.14	2	8	1	29.76	6.01	2	8	2	23.54	18.08	2	3	5	90.60	112.46
0	6	0	209.99	238.35	2	9	1	35.55	50.42	2	9	2	37.54	23.26	2	4	5	80.25	3.33
0	7	0	19.07	22.89	2	10	1	20.18	5.77	2	10	2	50.92	8.03	2	5	5	35.50	14.23
0	8	0	46.48	58.23	2	11	1	23.02	2.98	2	11	2	60.62	50.70	2	6	5	130.78	90.69
0	9	0	73.60	58.06	2	12	1	40.54	33.00	2	12	2	10.61	44.11	2	7	5	33.52	11.78
0	10	0	24.53	46.20	3	0	1	82.70	71.26	3	0	2	162.52	271.51	2	8	5	25.27	27.50
0	12	0	91.78	75.22	3	1	1	40.86	16.39	3	1	2	60.59	48.98	2	9	5	59.59	68.78
0	13	0	24.24	18.66	3	2	1	97.86	103.49	3	2	2	60.78	46.07	2	10	5	53.71	18.63
1	1	0	85.13	48.93	3	3	1	10.03	31.41	3	3	2	173.02	134.87	2	11	5	10.43	3.4
1	2	0	16.11	.25	3	4	1	60.81	14.17	3	4	2	41.43	39.42	2	12	5	38.33	30.51
1	3	0	38.13	9.00	3	5	1	105.57	84.04	3	5	2	51.47	57.39	3	0	5	17.29	5.61
1	4	0	53.21	17.09	3	6	1	71.19	60.19	3	6	2	142.91	103.81	3	1	5	71.74	42.81
1	5	0	10.77	4.18	3	7	1	71.34	22.39	3	7	2	43.07	10.86	3	2	5	69.99	44.39
1	6	0	43.30	54.31	3	8	1	90.48	56.85	3	8	2	57.49	65.79	3	3	5	27.44	31.19
1	7	0	32.76	56.09	3	9	1	23.92	15.93	3	9	2	89.51	41.04	3	4	5	42.28	12.56
1	8	0	54.09	8.42	3	10	1	51.52	32.32	3	10	2	25.37	15.03	3	5	5	68.88	64.01
1	9	0	27.49	30.41	3	11	1	50.36	33.41	3	11	2	24.57	37.29	3	6	5	28.42	17.49
2	1	0	28.97	61.55	4	0	1	57.38	44.53	4	0	2	154.22	75.01	3	0	0	0	140.51
2	2	0	16.11	.25	4	1	1	64.94	12.56	4	1	2	110.53	28.22	3	7	5	32.09	43.71
2	3	0	161.69	274.47	4	2	1	22.59	26.25	4	2	2	44.17	84.05	3	8	5	71.74	44.74
2	4	0	27.42	18.26	4	3	1	52.28	15.48	4	3	2	39.42	22.48	3	9	5	0	23.41
2	5	0	24.09	14.12	4	4	1	30.56	63.60	4	4	2	62.60	41.90	3	10	5	37.44	39.31
2	6	0	59.57	54.73	4	5	1	70.75	39.97	4	5	2	57.57	5.28	3	11	5	17.54	9.40
2	7	0	35.62	13.74	4	6	1	35.55	16.95	4	6	2	40.45	35.41	4	0	5	130.75	53.59
2	8	0	46.11	7.69	4	7	1	46.20	43.57	4	7	2	70.48	45.51	4	1	5	30.19	30.16
2	9	0	174.99	141.45	4	8	1	27.95	47.61	4	8	2	53.48	54.70	4	2	5	84.48	37.67
3	0	0	86.61	48.66	4	9	1	32.72	.61	4	9	2	33.21	5.15	4	3	5	47.24	39.16
3	1	0	90.16	146.51	4	10	1	42.25	25.68	4	10	2	17.34	12.23	4	4	5	29.80	5.11
3	2	0	38.13	9.00	5	0	1	110.24	68.09	5	0	2	63.15	12.85	4	5	5	62.73	64.70
3	3	0	27.42	18.26	5	1	1	82.70	36.13	5	1	2	70.29	9.20	4	6	5	62.08	1.45
3	4	0	146.02	207.75	5	2	1	42.42	.39	5	2	2	130.16	120.23	4	7	5	28.07	18.99
3	5	0	33.11	27.23	5	3	1	117.22	111.74	5	3	2	50.76	51.98	4	8	5	70.31	44.91
3	6	0	52.76	6.93	5	4	1	71.68	22.22	5	4	2	57.57	17.84	4	9	5	20.80	12.19
3	7	0	71.39	66.36	5	5	1	43.37	19.30	5	5	2	123.92	69.43	4	10	5	25.48	14.37
3	8	0	41.38	18.83	5	6	1	114.43	85.13	5	6	2	41.61	31.73	5	0	5	12.12	127.26
3	9	0	50.55	5.56	5	7	1	66.09	19.08	5	7	2	30.06	24.26	5	1	5	80.37	38.04
4	0	0	43.30	3.66	5	8	1	32.72	13.17	5	8	2	80.53	75.57	5	2	5	39.77	17.32
4	1	0	53.21	17.09	5	9	1	60.34	25.08	5	9	2	30.44	22.51	5	3	5	82.13	128.59
4	2	0	24.09	14.12	6	0	1	24.66	52.77	6	0	2	12.41	.78	5	4	5	50.26	14.78
4	3	0	33.11	27.23	6	1	1	23.51	1.78	6	1	2	54.21	5.62	5	5	5	0	7.80
4	4	0	229.24	201.23	6	2	1	61.49	52.45	6	2	2	73.00	58.77	5	6	5	16.23	53.99
4	5	0	39.61	67.47	6	3	1	53.76	29.85	6	3	2	144.57	76.07	5	7	5	20.66	.71
4	6	0	34.14	14.15	6	4	1	32.35	20.95	6	4	2	45.45	34.92	5	8	5	0	32.55
4	7	0	30.65	36.60	6	5	1	102.59	54.80	6	5	2	37.96	19.81	5	9	5	54.39	52.92
4	8	0	77.07	74.07	6	6	1	32.06	33.97	6	6	2	39.60	17.90	6	0	5	30.19	14.52
5	0	0	43.90	81.14	6	7	1	30.66	23.32	6	7	2	25.55	29.40	6	1	5	60.80	49.76
5	1	0	18.77	4.18	6	8	1	32.39	17.51	6	8	2	30.06	18.67	6	2	5	119.59	76.26
5	2	0	55.57	54.73	7	0	1	44.23	19.37	7	0	2	43.82	45.45	6	3	5	16.27	23.46
5	3	0	52.76	6.93	7	1	1	40.36	13.67	7	1	2	113.52	58.04	6	4	5	71.74	21.62
5	4	0	39.61	67.47	7	2	1	50.08	30.90	7	2	2	40.70	50.43	6	5	5	10.23	22.23
5	5	0	76.14	105.44	7	3	1	41.27	.19	7	3	2	49.99	62.62	6	6	5	16.82	8.19
5	6	0	49.51	36.83	7	4	1	50.57	25.47	7	4	2	70.48	61.35	6	7	5	32.73	34.45
5	7	0	55.28	65.71	7	5	1	64.12	29.26	7	5	2	29.19	16.56	6	8	5	46.81	23.39
6	0	0	208.99	238.35	7	6	1	40.12	11.27	7	6	2	31.21	46.19	7	0	5	80.76	20.76
6	1	0	43.30	54.31	7	7	1	36.33	40.32	7	7	2	61.32	30.52	7	1	5	27.44	23.48
6	2	0	35.62	13.74	8	0	1	80.56	119.69	8	0	2	93.26	19.88	7	2	5	33.52	31.80
6	3	0	71.39	66.36	8	1	1	79.08	37.55	8	1	2	15.88	2.96	7	3	5	39.09	.91
6	4	0	34.14	14.15	8	2	1	33.37	4.05	8	2	2	23.54	5.44	7	4	5	13.45	20.92
6	5	0	49.51	36.83	8	3	1	88.12	49.58	8	3	2	62.42	35.36	7	5	5	20.56	42.19
6	6	0	155.78	115.33	8	4	1	22.85	12.02	8	4	2	50.48	.00	7	6	5	32.93	4.96
6	7	0	19.07	22.89	8	5	1	26.44	17.71	8	5	2	84.50	65.25	7	7	5	16.43	27.55
6	8	0	32.96	56.09	8	6	1	36.17	50.75	8	6	2	29.00	10.72	8	0	5	144.27	99.83
6	9	0	46.11	7.69	9	0	1	50.97	27.40	9	0	2	80.34	88.35	8	1	5	29.30	2.08
7	0	0	41.38	18.83	9	1	1	34.20	12.25	9	1	2	51.10	11.44	8	2	5	29.29	25.84
7	1	0	30.65	36.60	9	2	1	38.80	27.97	9	2	2	30.48	8.96	8	3	5	87.03	89.43
7	2	0	46.48	58.23	9	3	1	28.11	33.47	9	3	2	89.51	36.34	8	4	5	68.41	24.23
7	3	0	54.09	8.42	9	4	1	30.66	20.19	9	4	2	29.37	27.63	8	5	5	19.01	30.69
7	4	0	174.99	141.45	9	5	1	39.46	32.11	9	5	2	39.22	21.67	8	6	5	69.00	48.12
7	5	0	50.55	5.56	10	0	1	22.19	20.97	10	0	2	24.64	71.51	9	1	5	40.97	38.78
7	6	0	59.28	65.71	10	1	1	27.95	26.34	10	1	2	87.24	53.46	9	2	5	50.26	16.92
7	7	0	73.60	58.06	10	2	1	23.18	34.34	10	2	2	47.54	39.69	9	3	5	19.01	23.76
7	8	0	27.49	30.41	10	3	1	43.24	28.50	10	3	2	29.37	41.90	9	4	5	20.66	21.28
7	9	0	86.61	43.66	10	4	1	22.52	34.89	10	4	2	17.34	14.48	9	5	5	31.76	17.61
8	0	0	24.53	46.20	11	0	1	71.02	69.57	11	0	2	40.15	3.07	10	0	5	50.06	5.52
8	1	0	26.97	61.55	11	1	1	43.40	34.11	11	1	2	10.07	4.73	10	1	5	26.95	3.98
8	2	0	79.07	74.07	11	2	1	20.11	1.52	11	2	2	63.88	83.27	10	2			

TABLE A3.2 (CONT.)

F(OBS), F(CALC) FOR $K_3[Mo(CNS)_6] \cdot 4H_2O$

1	9	4	55.19	21.39
1	10	4	39.97	24.02
1	11	4	39.14	37.27
1	12	4	29.66	19.90
2	0	4	28.69	68.03
2	1	4	64.67	40.44
2	2	4	94.33	74.78
2	3	4	104.73	79.63
2	4	4	44.73	4.16
2	5	4	30.39	57.34
2	6	4	57.36	37.78
2	7	4	72.45	25.22
2	8	4	85.82	66.21
2	9	4	45.71	70.83
2	10	4	32.33	21.14
2	11	4	30.38	51.26
2	12	4	19.69	17.73
3	0	4	118.15	117.45
3	1	4	107.94	93.51
3	2	4	83.88	70.73
3	3	4	78.04	68.36
3	4	4	59.81	33.19
3	5	4	55.49	78.59
3	6	4	27.23	37.78
3	7	4	57.86	2.68
3	8	4	60.29	61.48
3	9	4	32.58	10.68
3	10	4	49.84	6.64
3	11	4	45.71	25.83
4	0	4	77.55	3.45
4	1	4	14.34	35.70
4	2	4	44.73	7.58
4	3	4	51.78	45.52
4	4	4	72.94	79.50
4	5	4	28.69	82.86
4	6	4	22.64	31.68
4	8	4	39.87	12.54
4	9	4	50.33	30.37
4	10	4	47.16	39.80
5	0	4	122.77	4.55
5	1	4	103.08	51.17
5	2	4	30.39	3.50
5	3	4	65.64	29.94
5	4	4	28.69	22.38
5	6	4	55.19	15.07
5	7	4	39.87	9.97
5	8	4	5.33	31.82
5	9	4	52.51	18.94
6	0	4	153.16	141.69
6	1	4	95.03	75.82
6	2	4	51.05	26.20
6	3	4	35.50	65.37
6	4	4	21.64	10.31
6	5	4	39.14	26.43
6	6	4	56.16	42.81
6	7	4	39.38	24.94
6	8	4	43.27	39.32
7	0	4	65.64	98.38
7	2	4	69.29	49.74
7	3	4	48.87	47.07
7	4	4	22.61	3.92
7	5	4	42.95	33.65
7	6	4	32.09	49.40
7	7	4	21.64	21.91
8	0	4	77.07	39.26
8	1	4	60.54	18.42
8	2	4	91.41	84.84
8	3	4	75.37	12.69
8	4	4	39.87	9.73
8	5	4	39.38	53.99
8	6	4	37.58	.10
9	0	4	31.12	14.64
9	1	4	59.56	45.25
9	2	4	45.71	42.86
9	3	4	32.58	21.85
9	4	4	50.33	15.04
9	5	4	43.03	18.37
10	0	4	32.33	65.55
10	1	4	39.57	33.49
10	2	4	39.53	8.29
10	3	4	44.49	55.79
10	4	4	47.16	38.76
11	0	4	60.54	.15
11	1	4	39.14	4.59
11	2	4	30.88	9.78
11	3	4	50.08	11.18
12	0	4	53.73	42.65
12	1	4	29.66	35.01
13	0	4	19.94	70.88
13	1	4	18.48	34.08

F(OBS) FOR $K_3[Cr(NCS)_6] \cdot 4H_2O$ (Weak Layer-line data $\times 10^2$)

H	K	L	FOBS	H	K	L	FOBS
1	1	1	80	13	7	3	119
1	3	1	51	15	3	3	114
1	5	1	55	1	1	5	43
1	7	1	55	1	3	5	107
1	9	1	164	1	5	5	60
1	11	1	99	1	7	5	144
1	13	1	80	1	13	5	156
1	15	1	80	1	15	5	162
1	17	1	96	1	19	5	198
3	1	1	51	3	1	5	102
3	7	1	84	3	3	5	117
3	15	1	211	3	9	5	78
5	1	1	102	3	13	5	97
5	5	1	107	3	15	5	181
5	7	1	134	5	1	5	91
5	13	1	90	5	5	5	110
7	1	1	119	5	7	5	63
7	3	1	157	5	9	5	85
7	7	1	242	5	11	5	200
7	13	1	193	5	13	5	116
7	19	1	187	5	15	5	90
9	1	1	162	5	17	5	148
9	3	1	137	7	1	5	114
9	5	1	116	7	3	5	131
9	7	1	97	7	13	5	123
9	9	1	105	7	17	5	134
9	13	1	141	9	1	5	59
11	1	1	127	9	3	5	118
11	3	1	77	9	7	5	93
11	5	1	128	9	9	5	82
11	7	1	89	9	11	5	88
11	9	1	95	9	15	5	119
11	11	1	235	11	1	5	67
13	5	1	108	11	3	5	111
17	3	1	100	11	7	5	83
19	1	1	161	11	11	5	129
1	3	3	74	13	1	5	74
1	5	3	57	13	3	5	109
1	7	3	55	13	5	5	103
1	9	3	135	13	7	5	152
1	15	3	177	13	9	5	94
1	19	3	146	13	13	5	98
3	1	3	59	13	17	5	123
3	3	3	55	15	3	5	147
3	7	3	106	17	5	5	132
5	1	3	47	1	1	7	60
5	3	3	99	1	3	7	77
5	5	3	60	1	7	7	47
5	7	3	67	1	9	7	115
5	9	3	75	1	13	7	68
5	11	3	102	1	15	7	131
7	1	3	147	3	3	7	49
7	3	3	106	3	5	7	45
7	11	3	126	3	7	7	52
9	5	3	141	3	9	7	86
9	11	3	117	3	11	7	212
11	3	3	77	3	17	7	146
11	9	3	152	5	3	7	86
11	15	3	133	5	9	7	64
13	3	3	171	5	11	7	70
13	5	3	91	5	13	7	76
				5	15	7	155
				7	3	7	122
				7	7	7	120
				7	15	7	149
				9	1	7	69
				9	3	7	59
				11	1	7	108
				11	3	7	65
				11	5	7	102
				13	1	7	99
				13	5	7	111
				15	5	7	103
				1	1	9	88
				1	3	9	66
				1	5	9	39
				1	7	9	55
				1	11	9	70
				1	13	9	88
				1	15	9	70
				3	9	9	102
				3	15	9	110
				5	3	9	52
				5	5	9	112
				5	7	9	93
				7	1	9	46
				7	3	9	60
				7	5	9	83
				7	7	9	137
				9	1	9	101
				9	3	9	85
				9	5	9	61
				11	1	9	80
				11	3	9	62
				13	1	9	65

TABLE A3.4

F(OBS), F(CALC) FOR $K_2[MoCl_5H_2O]$ (UNOBSERVED REFLECTIONS MARKED*)

H	K	L	F _O	K+F _C	H	K	L	F _O	K+F _C	H	K	L	F _O	K+F _C	H	K	L	F _O	K+F _C
H= 0, L= 1					H= 3, L= 2					H= 6, L= 2					H= 10, L= 3				
0	1	1	-504	-512	3	0	2	484	544	6	0	2	229	201	10	1	3	120	114
0	3	1	231	260	3	1	2	-166	-127	6	1	2	-243	-231	H= 10, L= 4				
H= 0, L= 2					3	2	2	-175	-159	6	2	2	-131	-112	10	0	4	141	112
0	0	2	-200	-165	3	3	2	82	75	6	3	2	133	141	H= 11, L= 1				
0	2	2	-222	-196	3	4	2	442	460	H= 6, L= 3					11	1	1	162	145
0	4	2	-205	-172	H= 3, L= 3					6	0	3	-97	-83	11	2	1	-137	-115
H= 0, L= 3					3	1	3	-354	-370	6	2	3	-80	-67	11	3	1	-96	-93
0	1	3	97	74	3	2	3	216	205	6	4	3	-101	-81	H= 11, L= 2				
H= 0, L= 4					3	3	3	222	220	6	2	4	-225	-207	11	2	2	-172	-174
0	0	4	-233	-196	H= 3, L= 4					H= 6, L= 4					H= 11, L= 3				
0	2	4	-127	-110	3	0	4	-260	-260	6	1	5	-136	-135	11	0	3	122	108
0	4	4	-205	-178	3	1	4	132	144	6	2	5	-136	-135	11	1	3	-250	-272
H= 0, L= 5					3	4	4	-263	-252	H= 6, L= 5					11	3	3	137	174
0	1	5	125	111	H= 3, L= 5					6	0	6	-71	-22	H= 11, L= 4				
H= 0, L= 6					3	1	5	182	185	6	1	6	172	199	11	0	4	-165	-195
0	4	6	150	184	3	3	5	-130	-114	H= 7, L= 1					11	2	4	170	164
H= 1, L= 1					3	4	5	130	138	7	0	1	208	209	H= 12, L= 0				
1	0	1	-43	-24	H= 3, L= 6					7	1	1	-121	-105	12	1	0	-166	-177
1	1	1	130	118	3	1	6	-121	-134	7	3	1	91	63	12	3	0	137	112
1	2	1	105	91	H= 4, L= 0					H= 7, L= 2					H= 12, L= 1				
1	3	1	-67	-66	4	0	0	-313	-342	7	0	2	-173	-140	12	0	1	-221	-249
1	4	1	-55	-29	4	2	0	-417	-431	7	4	2	-146	-140	H= 12, L= 2				
H= 1, L= 2					4	4	0	-325	-314	H= 7, L= 3					12	1	2	122	136
1	0	2	249	223	H= 4, L= 1					7	1	3	191	182	H= 14, L= 1				
1	1	2	153	142	4	0	1	-323	-344	7	2	3	-181	-190					
1	2	2	334	365	4	1	1	277	272	7	3	3	-136	-112					
1	3	2	-90	-81	4	2	1	-65	-63	H= 7, L= 4									
1	4	2	238	201	4	3	1	-158	-160	7	0	4	280	252					
H= 1, L= 3					4	4	1	-281	-283	7	2	4	-132	-126					
1	0	3	244	248	H= 4, L= 2					7	4	4	208	253					
1	1	3	-195	-177	4	0	2	472	469	H= 7, L= 5									
1	2	3	-216	-213	4	1	2	169	150	7	1	5	-269	-280					
1	3	3	117	106	4	2	2	-221	-214	7	3	5	176	177					
1	4	3	247	229	4	3	2	-88	-85	H= 7, L= 6									
H= 1, L= 4					4	4	2	401	409	7	0	6	-211	-167					
1	0	4	-382	-331	H= 4, L= 3					H= 8, L= 0									
1	1	4	-350	-330	4	1	3	-235	-205	8	0	0	418	407					
1	2	4	128	122	4	3	3	138	123	8	1	0	316	288					
1	3	4	211	201	H= 4, L= 4					8	2	0	-203	-215					
1	4	4	-329	-311	4	0	4	115	94	8	3	0	-188	-173					
H= 1, L= 5					4	2	4	150	122	8	4	0	323	386					
1	0	5	-209	-218	4	4	4	104	84	H= 8, L= 1									
1	1	5	148	155	H= 4, L= 5					8	0	1	280	281					
1	3	5	-110	-96	4	1	5	-131	-124	8	1	1	-327	-320					
1	4	5	-209	-213	H= 4, L= 6					8	2	1	133	107					
H= 1, L= 6					4	0	6	-167	-194	8	3	1	211	200					
1	2	6	-164	-169	4	4	6	-171	-197	8	4	1	201	263					
1	4	6	116	85	H= 5, L= 1					H= 8, L= 2									
H= 2, L= 0					5	0	1	158	154	8	0	2	-117	-101					
2	1	0	-495	-538	5	1	1	-183	-168	8	1	2	-102	-74					
2	2	0	-25	-16	5	3	1	102	100	H= 8, L= 3									
2	3	0	240	293	5	4	1	161	139	8	2	3	151	138					
H= 2, L= 1					H= 5, L= 2					8	0	5	-141	-144					
2	0	1	-284	-304	5	0	2	-391	-395	H= 9, L= 1									
2	1	1	-99	-75	5	1	2	-358	-376	9	0	1	-170	-163					
2	2	1	228	251	5	3	2	228	223	9	1	1	-143	-133					
2	3	1	60	39	5	4	2	-385	-347	9	3	1	87	81					
2	4	1	-276	-253	H= 5, L= 3					H= 9, L= 2									
H= 2, L= 2					5	0	3	-299	-281	9	1	2	126	122					
2	1	2	260	267	5	1	3	153	126	9	2	2	127	97					
2	2	2	-92	-85	5	2	3	75	59	9	3	2	-90	-76					
2	3	2	-172	-153	5	3	3	-109	-81	H= 9, L= 3									
H= 2, L= 3					5	4	3	-282	-267	9	0	3	306	328					
2	0	3	286	293	H= 5, L= 4					9	2	3	-116	-105					
2	1	3	-90	-66	5	0	4	104	89	H= 9, L= 4									
2	4	3	274	259	5	1	4	143	159	9	1	4	-316	-312					
H= 2, L= 4					5	3	4	-123	-96	9	3	4	189	199					
2	0	4	242	216	H= 5, L= 5					H= 10, L= 0									
2	2	4	-165	-127	5	2	5	259	269	10	0	0	151	145					
2	4	4	211	195	5	4	5	-159	-149	10	1	0	-248	-220					
H= 2, L= 5					5	0	5	256	271	10	2	0	-189	-224					
2	1	5	-126	-107	H= 5, L= 6					10	3	0	153	143					
2	2	5	-180	-169	5	1	6	-167	-175	10	4	0	153	149					
H= 2, L= 6					H= 6, L= 0					H= 10, L= 1									
2	0	6	139	95	6	0	0	-77	-64	10	0	1	-129	-127					
2	2	6	-120	-101	6	1	0	242	240	10	1	1	-130	-123					
2	4	6	134	94	6	2	0	180	170	10	2	1	113	85					
H= 3, L= 1					6	3	0	-148	-145	10	3	1	97	73					
3	0	1	77	76	H= 6, L= 1					10	4	1	-154	-130					
3	1	1	138	117	6	0	1	252	279										
3	2	1	-276	-333	6	1	1	220	196										
3	3	1	-81	-66	6	2	1	-251	-252										
3	4	1	71	58	6	3	1	-128	-117										
					6	4	1	252	261										

TABLE A3.5

F(OBS), F(CALC) FOR (NH₄)₂[MoCl₅H₂O] (UNOBSERVED REFLECTIONS MARKED*)

H	K	L	F _O	K*F _C	H	K	L	F _O	K*F _C	H	K	L	F _O	K*F _C	H	K	L	F _O	K*F _C
H= 0, L= 0					H= 3, L= 1					H= 5, L= 2					H= 7, L= 3				
0	2	0	-407	-459	3	0	1	231	236	5	2	3	79	66	8	7	1	209	219
0	6	0	-354	-318	3	1	1	156	117	5	4	3	-121	-106	8	8	1	203	208
0	8	0	561	555	3	2	1	-238	-231	5	5	3	118	99	8	9	1	-183	-215
0	10	0	-236	-230	3	3	1	-111	-96	5	7	3	-94	-87	H= 8, L= 2				
H= 0, L= 1					3	4	1	211	176	5	9	3	88	81	8	0	2	-111	-111
0	3	1	366	397	3	5	1	121	110	H= 5, L= 4					8	1	2	-97	-77
0	5	1	-403	-382	3	6	1	-168	-145	5	1	4	103	103	8	4	2	-89	-106
0	7	1	288	268	3	7	1	-91	-76	5	3	4	-88	-89	8	5	2	-115	-85
0	9	1	-306	-286	3	8	1	138	125	5	5	4	103	108	H= 6, L= 0				
0	11	1	154	192	H= 3, L= 2					6	0	0	-231	-236	8	0	3	-177	-151
H= 0, L= 2					3	0	2	634	676	6	1	0	195	185	8	2	3	101	103
0	2	2	-240	-243	3	1	2	-180	-135	6	2	0	62	62	8	4	3	-142	-135
0	4	2	-175	-178	3	2	2	-193	-212	H= 6, L= 1					H= 9, L= 1				
0	6	2	-127	-80	3	3	2	147	114	6	3	0	-175	-161	9	0	1	-210	-206
0	8	2	-201	-146	3	4	2	456	520	6	4	0	-224	-203	9	1	1	-139	-117
H= 0, L= 3					3	5	2	-158	-120	6	5	0	187	179	9	3	1	110	103
0	1	3	50	39	3	6	2	-182	-175	6	6	0	-138	-126	9	4	1	-162	-180
0	3	3	-65	-35	3	7	2	92	65	6	7	0	-179	-160	9	5	1	-97	-96
H= 0, L= 4					3	8	2	337	348	6	8	0	185	152	9	6	1	-132	-134
0	4	4	-104	-69	3	9	2	-119	-96	H= 6, L= 2					H= 9, L= 2				
H= 1, L= 1					H= 3, L= 3					6	0	1	420	433	9	0	2	-85	-79
1	1	1	134	111	3	0	3	-166	-120	6	1	1	203	178	9	1	2	105	109
1	3	1	-96	-88	3	1	3	-307	-314	6	2	1	-231	-222	9	2	2	87	60
1	4	1	-123	-116	3	2	3	285	271	6	3	1	-167	-148	9	4	2	-94	-72
1	5	1	115	87	3	3	3	-152	-112	6	4	1	371	368	9	5	2	118	116
1	7	1	-63	-58	3	4	3	-293	-273	6	5	1	178	164	H= 9, L= 3				
1	8	1	-96	-80	3	5	3	85	76	6	6	1	-188	-183	9	0	3	385	380
H= 1, L= 2					3	6	3	202	197	6	7	1	-119	-108	9	2	3	-125	-117
1	1	2	103	129	3	7	3	-115	-92	6	8	1	249	276	9	4	3	290	346
1	2	2	248	279	3	8	3	-203	-216	6	9	1	136	135	9	6	3	-94	-114
1	3	2	-106	-104	H= 3, L= 4					6	0	2	291	255	9	8	3	252	273
1	4	2	145	115	3	0	4	-193	-225	6	1	2	-271	-240	H= 9, L= 4				
1	5	2	145	135	3	1	4	83	89	6	2	2	-152	-112	9	1	4	-221	-235
1	6	2	158	124	3	4	4	-88	-79	6	3	2	206	214	9	3	4	216	216
1	7	2	-90	-83	3	5	4	-192	-200	6	4	2	230	213	9	5	4	-217	-217
1	8	2	142	83	H= 4, L= 0					6	5	2	-222	-212	H= 10, L= 0				
1	9	2	119	116	4	0	0	-245	-220	6	6	2	-92	-85	10	0	0	265	291
H= 1, L= 3					4	2	0	-357	-339	6	7	2	181	165	10	1	0	-227	-211
1	1	3	-122	-145	4	4	0	-214	-196	6	8	2	190	152	10	2	0	-146	-115
1	2	3	-131	-131	4	6	0	-190	-130	6	9	2	-152	-170	10	3	0	205	197
1	3	3	150	126	4	8	0	-212	-156	H= 6, L= 3					10	4	0	268	262
1	4	3	310	315	H= 4, L= 1					6	1	3	-68	-66	10	5	0	-189	-189
1	5	3	-152	-138	4	0	1	-351	-351	6	3	3	75	58	10	6	0	-100	-97
1	6	3	-130	-120	4	1	1	266	260	H= 6, L= 4					10	7	0	159	160
1	7	3	90	96	4	3	1	-220	-222	6	0	4	113	94	10	8	0	207	204
1	8	3	271	239	4	4	1	-262	-263	6	2	4	-126	-91	10	9	0	-172	-152
1	9	3	-131	-115	4	5	1	237	240	6	4	4	100	83	H= 10, L= 1				
H= 1, L= 4					4	7	1	-184	-169	6	6	4	-89	-69	10	0	1	-207	-175
1	1	4	-162	-217	4	8	1	-192	-169	6	6	4	-89	-69	10	1	1	-165	-154
1	2	4	126	118	4	9	1	195	196	H= 7, L= 1					10	2	1	113	113
1	3	4	213	192	H= 4, L= 2					7	0	1	203	173	10	3	1	134	132
1	4	4	-293	-272	4	0	2	648	641	7	1	1	-138	-107	10	4	1	-154	-162
1	5	4	-205	-193	4	1	2	163	141	7	2	1	-90	-71	10	5	1	-157	-154
1	6	4	131	104	4	2	2	-293	-290	7	3	1	116	90	10	6	1	99	103
1	7	4	125	144	4	3	2	-139	-118	7	4	1	137	136	10	8	1	-108	-136
H= 2, L= 0					4	4	2	468	505	7	5	1	-89	-98	H= 10, L= 2				
2	0	0	48	32	4	5	2	129	113	H= 7, L= 2					10	0	2	-143	-142
2	1	0	-358	-420	4	6	2	-243	-222	7	0	2	-265	-251	10	1	2	91	98
2	3	0	280	333	4	7	2	-93	-78	7	1	2	102	75	10	4	2	-137	-134
2	5	0	-338	-332	4	8	2	338	339	7	2	2	-79	-70	H= 10, L= 3				
2	7	0	288	225	4	9	2	96	82	7	3	2	-218	-223	10	0	3	111	111
2	9	0	-292	-249	4	10	2	-108	-163	7	4	2	90	60	10	1	3	112	99
H= 2, L= 1					H= 4, L= 3					7	5	2	-180	-174	10	2	3	-92	-92
2	0	1	-485	-557	4	1	3	-233	-200	7	6	2	-180	-174	10	3	3	-93	-92
2	1	1	-114	-86	4	2	3	58	43	7	1	3	214	186	10	4	3	94	100
2	2	1	198	163	4	3	3	185	179	7	2	3	-150	-142	10	5	3	94	92
2	3	1	76	65	4	4	3	-182	-165	7	3	3	-168	-162	H= 11, L= 1				
2	4	1	-413	-434	4	5	3	152	134	7	4	3	176	185	11	1	1	179	153
2	5	1	-88	-67	4	7	3	-111	-125	7	5	3	-115	-111	11	2	1	-137	-132
2	6	1	164	158	H= 4, L= 4					7	6	3	-115	-131	11	3	1	-120	-142
2	8	1	-367	-310	4	9	3	-111	-125	7	7	3	-115	-131	11	5	1	140	144
H= 2, L= 2					4	2	4	74	55	7	8	3	133	165	H= 11, L= 2				
2	1	2	243	246	H= 5, L= 1					7	9	3	133	165	11	0	2	278	266
2	2	2	-76	-61	5	0	1	251	220	7	0	4	285	287	11	2	2	-136	-148
2	3	2	-190	-207	5	1	1	-167	-132	7	2	4	-129	-108	11	4	2	239	247
2	5	2	225	217	5	3	1	135	116	7	4	4	253	261	H= 11, L= 3				
2	7	2	-154	-152	5	4	1	199	183	7	6	4	-109	-101	11	0	3	133	144
2	9	2	160	172	5	5	1	-81	-98	7	7	4	-109	-101	11	1	3	-220	-250
H= 2, L= 3					5	8	1	157	139	8	0	0	447	492	11	3	3	204	230
2	0	3	200	211	H= 5, L= 2					8	0	0	261	251	11	4	3	114	129
2	1	3	-57	-60	5	0	2	-383	-360	8	1	0	-277	-279	11	5	3	-197	-234
2	2	3	-90	-92	5	1	2	-336	-355	8	2	0	-230	-218	H= 11, L= 4				
2	3	3	57	51	5	2	2	165	158	8	3	0	398	420	11	0	4	-181	-208
2	4	3	206	173	5	3	2	302	304	8	4	0	-216	-228	11	2	4	89	111
2	6	3	-83	-78	5	4	2	-203	-283	8	5	0	225	219	H= 12, L= 0				
2	8	3	140	124	5	5	2	-279	-298	8	6	0	-216	-228	12	1	0	-147	-145
H= 2, L= 4					5	6	2	147	128	8	7	0	-164	-156	12	3	0	122	129
2	0	4	113	131	5	7	2	206	216	8	8	0	307	308	1				

TABLE A3.6

F(OBS), F(CALC) FOR $\text{Rb}_2[\text{MoCl}_5\text{H}_2\text{O}]$ (UNOBSERVED REFLECTIONS MARKED*)

H	K	L	FO	K*FC	H	K	L	FO	K*FC	H	K	L	FO	K*FC	H	K	L	FO	K*FC
H= 0, L= 1					H= 2, L= 5					H= 5, L= 3					H= 8, L= 2				
0	1	1	-367	-402	2	0	5	-132	-106	5	1	2	-277	-283	8	3	1	184	187
0	3	1	247	269	2	1	5	-89	-96	5	2	2	-193	-179	8	4	1	254	271
0	5	1	-178	-207	2	2	5	-270	-272	5	4	2	-322	-354	8	5	1	-139	-137
H= 0, L= 2					H= 2, L= 6					H= 5, L= 4					H= 8, L= 3				
0	0	2	-241	-225	2	1	6	-98	-108	5	0	3	-232	-200	8	0	2	-121	-96
0	2	2	-319	-292	2	2	6	-138	-114	5	1	3	132	113	8	2	2	-83	-54
0	4	2	-220	-181	H= 2, L= 7					5	2	3	140	106	8	4	2	-85	-64
H= 0, L= 3					2	0	7	-98	-94	5	3	3	-107	-88	H= 8, L= 4				
0	1	3	61	45	H= 3, L= 1					5	4	3	-163	-164	8	2	3	109	115
0	3	3	-45	-32	3	0	1	-71	-50	5	5	3	79	64	H= 8, L= 5				
H= 0, L= 4					3	1	1	106	97	5	0	4	190	170	8	4	4	-94	-73
0	0	4	-258	-235	3	2	1	-341	-353	5	1	4	85	115	H= 8, L= 6				
0	2	4	-254	-239	3	3	1	-89	-65	5	2	4	207	162	8	0	5	-173	-203
0	4	4	-221	-189	3	4	1	-49	-48	5	4	4	143	143	8	2	5	-121	-128
H= 0, L= 5					3	5	1	72	59	5	5	4	87	81	8	4	5	-133	-172
0	1	5	88	71	H= 3, L= 2					5	0	5	177	188	H= 8, L= 7				
0	3	5	-63	-50	3	0	2	-520	501	5	2	5	-116	-91	8	0	6	97	127
H= 0, L= 6					3	1	2	-146	-113	5	4	5	145	163	H= 8, L= 8				
0	0	6	259	253	3	3	2	110	84	5	0	6	-141	-161	8	0	7	-161	-145
0	2	6	214	173	3	4	2	345	372	5	2	6	99	105	8	2	7	-84	-68
0	4	6	208	216	3	5	2	-86	-63	5	4	6	99	105	8	4	7	-134	-120
H= 0, L= 8					H= 3, L= 3					H= 6, L= 0					H= 9, L= 1				
0	0	8	-139	-119	3	0	3	187	158	6	1	0	191	181	9	0	1	-161	-145
H= 1, L= 1					3	1	3	-284	-274	6	2	0	270	256	9	1	1	-84	-68
1	0	1	58	51	3	2	3	376	348	6	3	0	-133	-135	9	4	1	-134	-120
1	1	1	129	96	3	3	3	198	199	6	5	0	111	114	H= 9, L= 2				
1	2	1	199	142	3	4	3	153	122	6	0	1	95	73	9	0	2	144	138
1	3	1	-78	-62	3	5	3	-179	-157	6	1	1	141	132	9	2	2	250	237
1	4	1	38	37	H= 3, L= 4					6	2	1	-298	-341	9	4	2	127	114
1	5	1	61	50	3	0	4	-253	-238	6	3	1	-103	-92	9	0	3	226	260
H= 1, L= 2					3	1	4	111	103	6	4	1	68	60	9	4	3	204	223
1	0	2	335	314	3	2	4	-112	-72	6	5	1	99	80	H= 9, L= 3				
1	1	2	107	98	3	3	4	-80	-79	6	0	2	125	93	9	0	4	-122	-140
1	2	2	435	460	3	4	4	-231	-199	6	1	2	-193	-191	9	2	5	-112	-124
1	3	2	-79	-66	3	5	4	83	63	6	2	2	-136	-139	H= 9, L= 4				
1	4	2	266	248	H= 3, L= 5					6	3	2	139	146	9	0	6	-121	-103
1	5	2	89	68	3	1	5	128	139	6	4	2	90	73	9	2	7	-228	-265
H= 1, L= 3					3	3	5	-129	-104	6	5	2	-117	-110	9	3	4	194	209
1	0	3	87	59	H= 3, L= 6					6	0	3	125	93	9	4	4	-116	-88
1	1	3	-144	-118	3	1	6	-99	-103	6	1	4	-198	-216	H= 9, L= 5				
1	2	3	-321	-285	H= 3, L= 7					6	2	4	-198	-216	10	1	0	-211	-190
1	4	3	80	45	3	0	7	-160	-167	6	3	5	137	154	10	2	0	-297	-301
1	5	3	-96	-78	H= 4, L= 0					6	4	6	141	143	10	3	0	168	155
H= 1, L= 4					4	0	0	-374	-428	6	5	6	141	143	10	5	0	-127	-110
1	0	4	-377	-381	4	2	0	-518	-604	6	0	7	141	143	H= 10, L= 1				
1	1	4	-276	-259	4	4	0	-314	-341	6	1	8	141	143	10	1	1	-128	-114
1	3	4	218	195	H= 4, L= 1					6	2	9	141	143	10	2	1	157	143
1	4	4	-337	-309	4	0	1	-297	-311	6	3	10	141	143	10	3	1	91	83
1	5	4	-175	-150	4	1	1	207	211	6	4	11	141	143	H= 10, L= 2				
H= 1, L= 5					4	2	1	-155	-150	6	5	12	141	143	10	4	4	133	135
1	0	5	-182	-155	4	3	1	-145	-148	6	0	13	141	143	H= 11, L= 1				
1	1	5	136	147	4	4	1	-213	-229	7	0	1	234	233	11	1	1	135	113
1	2	5	89	83	4	5	1	110	130	7	1	1	-87	-75	11	2	1	-179	-175
1	3	5	-138	-114	H= 4, L= 2					7	2	1	143	130	11	3	1	-95	-90
1	4	5	-147	-132	4	0	2	456	460	7	3	1	178	182	H= 11, L= 2				
1	5	5	89	90	4	1	2	140	117	7	4	1	178	182	11	2	2	-202	-200
H= 1, L= 6					4	2	2	-141	-112	7	0	2	-148	-109	H= 11, L= 3				
1	0	6	-154	-151	4	3	2	-95	-82	7	1	3	-173	-187	11	0	3	186	192
H= 1, L= 7					4	4	2	330	350	7	2	4	-112	-92	11	1	3	-199	-195
1	0	7	121	105	4	5	2	80	63	7	3	5	137	154	11	2	3	153	158
H= 1, L= 8					H= 4, L= 3					7	4	6	141	143	11	4	3	176	162
1	0	8	103	113	4	1	3	-183	-175	7	0	7	141	143	H= 11, L= 4				
H= 2, L= 0					4	3	3	154	135	7	1	8	141	143	11	1	4	138	151
2	1	0	-374	-401	4	4	3	-106	-95	7	2	9	141	143	11	2	4	-111	-95
2	2	0	-76	-52	H= 4, L= 4					7	3	10	141	143	H= 12, L= 0				
2	3	0	224	271	4	0	4	177	161	7	4	11	141	143	12	1	0	-121	-98
2	5	0	-137	-207	4	2	4	232	219	7	5	12	141	143	12	2	0	97	70
H= 2, L= 1					4	4	4	157	130	7	0	13	141	143	H= 12, L= 1				
2	0	1	-75	-49	H= 4, L= 5					7	1	14	141	143	12	0	1	-252	-297
2	1	1	-86	-64	4	0	5	113	114	7	2	15	141	143	12	1	2	-98	-96
2	2	1	433	424	4	1	5	-92	-88	7	3	16	141	143	12	2	3	-242	-254
2	3	1	59	40	4	2	5	168	133	7	4	17	141	143	H= 12, L= 2				
2	4	1	-30	-26	4	3	5	113	95	7	5	18	141	143	12	0	2	122	85
2	5	1	-44	-33	H= 4, L= 6					7	0	19	141	143	12	1	2	141	135
H= 2, L= 2					4	0	6	-269	-276	7	1	20	141	143	12	2	2	-99	-94
2	1	2	221	205	4	1	6	-99	-61	7	2	21	141	143	12	3	2	94	75
2	2	2	-156	-146	4	2	6	-223	-237	7	3	22	141	143	H= 12, L= 3				
2	3	2	132	119	H= 5, L= 1					7	4	23	141	143	12	1	3	-99	-124
H= 2, L= 3					5	0	1	108	89	7	5	24	141	143	H= 13, L= 1				
2	0	3	235	218	5	1	1	-113	-86	7	0	25	141	143	13	0	1	141	126
2	1	3	46	40	5	2	1	73	65	7	1	26	141	143	H= 13, L= 2				
2	2	3	191	171	5	3	1	87	69	7	2	27	141	143	H= 13, L= 3				
H= 2, L= 4					H= 5, L= 2					7	3	28	141	143	H= 13, L= 3				
2	0	4	199	158	5	0	2	-442	-454	7	4	29	141	143	H= 13, L= 3				
2	1	4	-95	-71	H= 5, L= 3					7	5	30	141	143	H= 13, L= 3				
2	2	4	149	125	H= 5, L= 4					7	6	31	141	143	H= 13, L= 3				

TABLE A3.7

F(OBS), F(CALC) FOR $\text{Rb}_2[\text{FeCl}_5\text{H}_2\text{O}]$ (UNOBSERVED REFLECTIONS MARKED*)

H	K	L	F0	K+F0	H	K	L	F0	K+F0	H	K	L	F0	K+F0	H	K	L	F0	K+F0
H= 0, L= 0					H= 3, L= 3					H= 6, L= 3					H= 10, L= 0				
0	2	0	259	200	3	0	3	301	267	6	1	2	-214	-193	10	0	0	-64	-77
0	6	0	154	139	3	1	3	-201	-191	6	2	2	-151	-146	10	1	0	-223	-215
0	8	0	751	763	3	2	3	358	384	6	3	2	186	157	10	2	0	-311	-288
H= 0, L= 1					3	3	3	140	143	6	4	2	80	60	10	3	0	201	192
0	1	1	-261	-368	3	4	3	264	237	6	5	2	-183	-166	10	5	0	-186	-189
0	3	1	237	256	3	5	3	-190	-172	6	6	2	-92	-103	10	6	0	-207	-213
0	5	1	-264	-279	3	6	3	261	273	6	9	2	-112	-122	10	7	0	136	140
0	7	1	140	137	3	8	3	163	149	H= 6, L= 3					H= 10, L= 1				
U	9	1	-186	-195	3	9	3	-129	-132	6	0	3	-82	-96	10	2	1	192	192
H= 0, L= 2					H= 3, L= 4					6	4	3	-58	-83	10	6	1	156	148
0	2	2	-482	-541	3	0	4	-282	-275	H= 6, L= 4					H= 10, L= 4				
0	4	2	-293	-237	3	1	4	50	61	6	0	4	-70	-13	10	0	4	198	215
0	6	2	-313	-312	3	2	4	-237	-221	6	2	4	-255	-234	10	4	4	216	189
0	8	2	-152	-151	3	4	4	-248	-233	6	6	4	-185	-178	H= 11, L= 1				
0	10	2	-171	-174	3	6	4	-160	-159	7	0	1	422	405	11	0	1	-135	-134
H= 0, L= 4					3	8	4	-139	-154	7	2	1	228	202	11	2	1	-296	-282
0	2	4	-234	-285	H= 4, L= 0					7	4	1	355	333	11	6	1	-225	-216
0	4	4	-251	-281	4	0	0	-571	-561	7	6	1	151	142	H= 11, L= 2				
0	6	4	-212	-201	4	2	0	-811	-940	7	8	1	205	218	11	2	2	-167	-158
0	8	4	-195	-188	4	4	0	-450	-453	7	0	2	-144	-137	H= 11, L= 3				
H= 1, L= 1					4	6	0	-601	-566	7	2	2	-137	-111	11	0	3	297	296
1	1	1	89	60	4	8	0	-296	-279	7	3	2	-80	-75	11	1	3	-133	-129
1	2	1	166	148	4	0	1	-546	-489	7	4	2	-120	-114	11	2	3	240	261
1	4	1	114	107	4	1	1	135	140	7	6	2	-95	-80	11	3	3	94	103
1	6	1	98	114	4	2	1	-305	-283	H= 7, L= 3					11	4	3	237	259
H= 1, L= 2					4	3	1	-62	-90	7	0	3	-280	-297	11	5	3	-128	-127
1	2	2	630	704	4	4	1	-389	-371	7	2	3	-465	-434	11	6	3	208	199
1	4	2	374	361	4	5	1	151	138	7	4	3	-251	-250	H= 12, L= 1				
1	6	2	405	437	4	6	1	-188	-180	7	6	3	-304	-327	12	0	1	-420	-479
1	8	2	210	216	4	8	1	-216	-224	7	8	3	-168	-158	12	2	1	-298	-291
1	10	2	214	253	4	10	1	-92	-99	7	0	4	279	255	12	4	1	-417	-420
H= 1, L= 3					4	0	2	698	716	7	2	4	235	225	12	6	1	-198	-220
1	1	3	-41	-54	4	1	2	86	80	7	4	4	159	162	12	0	2	138	142
1	2	3	-267	-262	4	2	2	-57	-47	H= 8, L= 0					H= 12, L= 2				
1	6	3	-191	-196	4	4	2	581	557	8	0	0	710	698	12	2	2	-298	-291
H= 1, L= 4					4	8	2	358	351	8	1	0	198	162	12	4	1	-417	-420
1	1	4	-146	-197	H= 4, L= 3					8	3	1	231	201	12	6	1	-198	-220
1	2	4	-87	-103	4	0	3	-75	-59	8	4	0	627	584	H= 8, L= 1				
1	3	4	152	155	4	1	3	-163	-158	8	5	0	175	149	8	0	1	498	516
1	4	4	-432	-450	4	3	3	173	136	8	1	1	-232	-233	8	2	1	452	420
1	5	4	-175	-178	4	4	3	-52	-47	8	3	1	231	201	8	4	1	449	435
1	8	4	-285	-303	4	5	3	-140	-129	8	5	1	-226	-201	8	6	1	314	302
1	9	4	-118	-135	H= 4, L= 4					8	7	1	99	138	8	8	1	252	287
H= 2, L= 0					4	0	4	201	228	8	9	1	-125	-150	8	0	2	-124	-125
2	0	0	-160	-129	4	2	4	298	274	8	1	1	-232	-233	8	2	2	-192	-166
2	1	0	-337	-336	4	4	4	219	189	8	3	1	231	201	8	4	2	-90	-109
2	3	0	227	220	4	6	4	200	207	8	5	1	-226	-201	8	6	2	-137	-120
2	4	0	-116	-99	4	8	4	123	117	8	6	1	314	302	8	8	2	-137	-120
2	5	0	-284	-264	H= 5, L= 1					8	7	1	99	138	8	0	2	-124	-125
2	7	0	110	107	5	0	1	124	103	8	8	1	252	287	8	2	2	-192	-166
2	9	0	-187	-187	5	1	1	-116	-105	8	9	1	-125	-150	8	4	2	-90	-109
H= 2, L= 1					5	4	1	74	78	8	6	2	-137	-120	8	6	2	-137	-120
2	0	1	125	74	H= 5, L= 2					8	0	2	-124	-125	8	8	2	-137	-120
2	1	1	-60	-52	5	0	2	-796	-739	8	2	2	-192	-166	8	0	4	-159	-136
2	2	1	527	517	5	1	2	-262	-261	8	4	2	-90	-109	8	2	4	-133	-123
2	4	1	109	90	5	2	2	-294	-260	8	6	2	-137	-120	8	4	4	-134	-120
2	6	1	359	371	5	3	2	205	200	8	8	2	-137	-120	8	6	4	-108	-89
2	10	1	177	214	5	4	2	-617	-598	H= 8, L= 3					H= 9, L= 1				
H= 2, L= 2					5	5	2	-240	-221	8	2	3	132	104	9	0	1	-203	-209
2	0	2	55	60	5	6	2	-168	-179	9	1	1	-104	-96	9	1	1	-104	-96
2	1	2	138	130	5	8	2	-378	-387	9	2	1	-61	-59	9	2	1	-61	-59
2	3	2	-78	-85	5	9	2	-163	-163	9	3	1	90	61	9	3	1	90	61
2	5	2	137	124	H= 5, L= 3					9	4	1	-205	-177	9	4	1	-205	-177
H= 2, L= 3					5	0	3	-221	-204	9	8	1	-93	-118	9	0	2	226	239
2	0	3	187	228	5	1	3	97	93	9	2	2	332	336	9	2	2	332	336
2	1	3	-63	-67	5	3	3	-100	-86	9	4	2	206	202	9	4	2	206	202
2	3	3	57	59	5	4	3	-189	-167	9	6	2	229	254	9	6	2	229	254
2	4	3	205	184	5	5	3	84	75	9	8	2	108	127	9	8	2	108	127
H= 2, L= 4					5	8	3	-114	-113	H= 9, L= 2					H= 9, L= 3				
2	0	4	195	211	H= 5, L= 4					9	0	3	266	288	9	0	3	266	288
2	2	4	-88	-96	5	0	4	242	242	9	2	3	89	93	9	2	3	89	93
2	4	4	198	175	5	2	4	326	278	9	4	3	241	254	9	4	3	241	254
2	8	4	108	120	5	4	4	220	206	9	8	3	185	179	9	8	3	185	179
H= 3, L= 1					5	6	4	221	208	H= 9, L= 4					H= 9, L= 4				
3	0	1	-140	-106	5	8	4	121	134	9	0	4	-202	-212	9	0	4	-202	-212
3	1	1	45	67	H= 6, L= 0					9	1	4	-212	-205	9	1	4	-212	-205
3	2	1	-451	-480	6	0	0	133	120	9	2	4	-87	-75	9	2	4	-87	-75
3	4	1	-114	-103	6	2	0	267	238	9	3	4	166	174	9	3	4	166	174
3	6	1	-315	-310	6	4	0	110	102	9	4	4	-196	-185	9	4	4	-196	-185
10	1	1	-175	-182	6	6	0	211	180	9	5	4	-177	-191	9	5	4	-177	-191
H= 3, L= 2					6	10	0	87	111	9	7	4	111	119	9	7	4	111	119
3	0	2	710	754	H= 6, L= 1					9	0	4	-202	-212	9	0	4	-202	-212
3	1	2	-112	-90	6	1	1	121	88	9	1	4	-212	-205	9	1	4	-212	-205
3	2	2	115	90	6	2	1	-437	-409	9	2	4	-87	-75	9	2	4	-87	-75
3	3	2	59	60	6	6	1	-319	-298	9	3	4	166	174	9	3	4	166	174
3	4	2	652	575	6	10	1	-160	-179	9	4	4	-196	-185	9	4	4	-196	-185
3	5	2	-76	-82	H= 6, L= 2					9	5	4	-177	-191	9	5	4	-177	-191
8	2	2	347	360	6	0	2	112	80	9	7	4	111	119	9	7	4	111	119

TABLE A3.8

F(OBS), F(CALC) FOR $\text{Cs}_2[\text{MoCl}_5\text{H}_2\text{O}]$ (UNOBSERVED REFLECTIONS MARKED*)

H	K	L	F _O	K+F _C	H	K	L	F _O	K+F _C	H	K	L	F _O	K+F _C
H= 0, L= 0					3	9	2	-252	-225	H= 0, L= 6				
0	4	0	129	98	3	17	2	-180	-186	0	0	6	-464	-501
0	6	0	-366	-438	H= 4, L= 2					0	4	6	-168	-189
0	8	0	705	787	4	0	2	-462	-441	0	8	6	-249	-272
0	14	0	-488	-469	4	4	2	-311	-302	0	10	6	100	108
0	16	0	170	127	4	6	2	107	92	0	14	6	162	195
H= 1, L= 0					4	8	2	-241	-228	H= 1, L= 6				
1	3	0	-379	-423	4	10	2	156	156	1	3	6	195	191
1	5	0	-337	-339	4	14	2	181	163	1	5	6	163	157
1	9	0	255	261	H= 0, L= 3					1	9	6	-122	-124
1	17	0	225	220	0	4	3	-182	-175	H= 2, L= 6				
H= 2, L= 0					0	6	3	-337	-317	2	0	6	-441	-435
2	2	0	-90	-96	0	8	3	-184	-164	2	4	6	-115	-123
2	4	0	556	641	0	10	3	-171	-163	2	6	6	96	112
2	6	0	-118	-105	0	14	3	-197	-164	2	8	6	-231	-240
2	8	0	320	303	H= 1, L= 3					2	14	6	176	172
2	10	0	-308	-277	1	3	3	439	427	H= 3, L= 6				
2	12	0	108	51	1	5	3	-94	-72	3	3	6	199	164
2	14	0	-231	-211	1	7	3	185	195	3	5	6	174	141
2	16	0	69	64	1	9	3	82	99	3	9	6	-133	-111
2	18	0	-166	-142	1	11	3	318	336	H= 4, L= 6				
H= 3, L= 0					H= 2, L= 3					4	0	6	-280	-302
3	1	0	-80	-151	2	2	3	265	227	4	4	6	-90	-99
3	3	0	-225	-248	2	6	3	-528	-464	4	8	6	-158	-169
3	5	0	-148	-151	2	8	3	-277	-251	4	14	6	104	123
3	9	0	126	125	2	14	3	-212	-195	H= 0, L= 7				
3	17	0	164	159	H= 3, L= 3					0	4	7	-71	-79
H= 4, L= 0					3	3	3	400	402	0	6	7	-141	-147
4	4	0	88	95	3	5	3	-99	-82	0	14	7	-89	-98
4	6	0	-203	-203	3	7	3	122	98	H= 1, L= 7				
4	8	0	387	399	3	11	3	294	315	1	3	7	169	200
4	14	0	-298	-270	H= 4, L= 3					1	11	7	153	174
4	16	0	85	77	4	4	3	-97	-84	H= 2, L= 7				
H= 0, L= 1					4	6	3	-206	-208	2	2	7	138	136
0	2	1	-270	-233	4	8	3	-100	-108	2	6	7	-259	-247
0	4	1	122	117	4	10	3	-62	-76	2	8	7	-150	-136
0	6	1	575	618	4	14	3	-107	-118	2	14	7	-111	-112
0	8	1	310	322	H= 0, L= 4					H= 3, L= 7				
0	10	1	109	84	0	0	4	988	928	3	3	7	211	203
0	14	1	265	253	0	4	4	154	174	3	11	7	143	173
H= 1, L= 1					0	6	4	-234	-239	H= 4, L= 7				
1	3	1	-520	-560	0	8	4	448	478	4	6	7	-84	-105
1	5	1	124	95	0	10	4	-93	-94	H= 0, L= 8				
1	7	1	-191	-209	0	14	4	-346	-322	0	0	8	285	297
1	9	1	-89	-115	H= 1, L= 4					0	8	8	125	167
1	11	1	-431	-408	1	3	4	-317	-281	H= 1, L= 8				
1	17	1	69	50	1	5	4	-266	-230	1	3	8	-136	-124
H= 2, L= 1					1	9	4	206	182	1	5	8	-115	-106
2	2	1	-46	-26	1	17	4	175	171	H= 2, L= 8				
2	4	1	146	133	H= 2, L= 4					2	0	8	266	285
2	6	1	388	385	2	0	4	598	523	2	8	8	131	163
2	8	1	198	202	2	4	4	315	312	H= 3, L= 8				
2	10	1	130	113	2	6	4	-80	-113	3	3	8	-106	-111
2	14	1	217	188	2	8	4	252	270	H= 4, L= 8				
H= 3, L= 1					2	10	4	-189	-162					
3	3	1	-370	-403	2	14	4	-178	-191					
3	5	1	97	68	H= 3, L= 4									
3	7	1	-178	-184	3	1	4	-102	-73					
3	11	1	-310	-319	3	3	4	-227	-205					
H= 4, L= 1					3	5	4	-166	-151					
4	2	1	-120	-108	3	9	4	128	118					
4	4	1	51	64	H= 4, L= 4									
4	6	1	309	329	4	0	4	500	497					
4	8	1	171	177	4	4	4	96	98					
4	10	1	58	41	4	6	4	-141	-132					
4	14	1	161	154	4	8	4	272	272					
H= 0, L= 2					4	14	4	-174	-192					
0	0	2	-890	-738	H= 0, L= 5									
0	2	2	114	109	0	2	5	-227	-249					
0	4	2	-710	-725	0	6	5	429	457					
0	6	2	132	129	0	8	5	235	251					
0	8	2	-374	-360	0	14	5	195	194					
0	10	2	309	311	H= 1, L= 5									
0	12	2	-91	-53	1	3	5	-367	-341					
0	14	2	232	248	1	5	5	61	67					
0	18	2	177	159	1	7	5	-91	-101					
H= 1, L= 2					1	11	5	-249	-277					
1	1	2	131	112	H= 2, L= 5									
1	3	2	349	330	2	4	5	135	100					
1	5	2	274	236	2	6	5	188	179					
1	9	2	-209	-190	2	8	5	94	90					
1	17	2	-194	-192	2	14	5	130	114					
H= 2, L= 2					H= 3, L= 5									
2	0	2	-1011	-1088	3	3	5	-255	-225					
2	4	2	-135	-122	3	7	5	-130	-128					
2	6	2	281	278	3	11	5	-169	-193					
2	8	2	-539	-532	H= 4, L= 5									
2	14	2	584	343	4	2	5	-142	-131					
2	16	2	-96	-95	4	6	5	277	259					
H= 3, L= 2					4	8	5	154	142					
3	1	2	-48	-5	4	14	5	106	118					
3	3	2	325	320										
3	5	2	310	266										

TABLE A3.9

F(OBS), F(CALC) FOR $\text{Cs}_2[\text{FeCl}_5\text{H}_2\text{O}]$ (UNOBSERVED REFLECTIONS MARKED*)

H	K	L	FO	K*FC
H= 0, L= 0				
0	4	0	176	158
0	6	0	-291	-335
0	8	0	510	603
0	10	0	-108	-109
0	14	0	-382	-423
0	16	0	100	78
H= 1, L= 0				
1	3	0	-296	-360
1	5	0	-238	-264
1	9	0	204	193
1	15	0	121	126
1	17	0	202	225
H= 2, L= 0				
2	2	0	-95	-93
2	4	0	517	610
2	6	0	-69	-51
2	8	0	216	197
2	10	0	-296	-316
2	12	0	108	79
2	14	0	-152	-151
2	18	0	-226	-235
H= 3, L= 0				
3	3	0	-164	-177
3	5	0	-52	-62
3	13	0	146	138
3	15	0	116	128
3	17	0	140	130
H= 4, L= 0				
4	4	0	113	128
4	6	0	-146	-143
4	8	0	280	283
4	10	0	-81	-80
4	14	0	-221	-231
H= 0, L= 1				
0	2	1	-119	-107
0	4	1	118	111
0	6	1	415	465
0	8	1	210	222
0	10	1	141	141
0	14	1	223	215
H= 1, L= 1				
1	1	1	81	46
1	3	1	-446	-484
1	5	1	63	57
1	7	1	-314	-317
1	9	1	-89	-113
1	11	1	-339	-388
H= 2, L= 1				
2	2	1	87	64
2	4	1	153	133
2	6	1	247	274
2	8	1	125	124
2	10	1	165	169
2	14	1	167	158
H= 3, L= 1				
3	1	1	83	70
3	3	1	-324	-310
3	7	1	-254	-267
3	9	1	-76	-84
3	11	1	-250	-270
H= 4, L= 1				
4	6	1	224	232
4	8	1	115	119
4	10	1	82	84
4	14	1	127	123
H= 0, L= 2				
0	0	2	-571	-528
0	2	2	125	104
0	4	2	-650	-680
0	6	2	76	68
0	8	2	-262	-238
0	10	2	359	350
0	12	2	-91	-84
0	14	2	184	181
0	18	2	228	260
H= 1, L= 2				
1	1	2	238	187
1	3	2	304	274
1	5	2	174	158
1	9	2	-133	-116
1	13	2	-117	-125
1	15	2	-122	-140
1	17	2	-165	-189
H= 2, L= 2				
2	0	2	-832	-846
2	4	2	-216	-173
2	6	2	234	215
2	8	2	-425	-414
2	10	2	102	107
2	14	2	348	318
H= 3, L= 2				
3	3	2	174	261

H	K	L	FO	K*FC
3	5	2	260	217
3	9	2	-178	-166
3	17	2	-176	-184
H= 4, L= 2				
4	0	2	-323	-303
4	4	2	-331	-296
4	8	2	-169	-143
4	10	2	170	181
4	14	2	109	119
H= 0, L= 3				
0	2	3	-221	-191
0	4	3	-218	-179
0	6	3	-235	-202
0	8	3	-110	-79
0	10	3	-279	-232
0	12	3	-116	-136
0	14	3	-173	-149
H= 1, L= 3				
1	1	3	-91	-81
1	3	3	408	370
1	7	3	385	315
1	9	3	117	99
1	11	3	354	321
H= 2, L= 3				
2	2	3	181	139
2	4	3	-65	-56
2	6	3	-397	-380
2	8	3	-239	-200
2	10	3	-62	-68
2	14	3	-207	-179
H= 3, L= 3				
3	3	3	334	347
3	7	3	197	168
3	9	3	85	78
3	11	3	304	299
H= 4, L= 3				
4	2	3	-65	-68
4	4	3	-109	-89
4	6	3	-141	-132
4	10	3	-125	-123
4	14	3	-87	-91
H= 0, L= 4				
0	0	4	741	719
0	4	4	249	238
0	6	4	-206	-178
0	8	4	446	366
0	10	4	-147	-145
0	14	4	-323	-294
H= 1, L= 4				
1	1	4	-126	-115
1	3	4	-278	-253
1	5	4	-207	-178
1	9	4	180	131
1	17	4	155	182
H= 2, L= 4				
2	0	4	460	416
2	4	4	332	338
2	6	4	-81	-78
2	8	4	244	201
2	10	4	-219	-204
2	14	4	-175	-165
H= 3, L= 4				
3	1	4	-159	-128
3	3	4	-181	-167
3	13	4	115	90
H= 4, L= 4				
4	0	4	359	367
4	4	4	143	139
4	6	4	-83	-91
4	8	4	215	194
4	10	4	-110	-90
4	14	4	-142	-167
H= 0, L= 5				
0	2	5	-191	-170
0	6	5	448	396
0	8	5	254	219
0	14	5	199	187
H= 1, L= 5				
1	3	5	-314	-334
1	7	5	-233	-207
1	9	5	-96	-83
1	11	5	-319	-297
H= 2, L= 5				
2	2	5	144	131
2	4	5	136	121
2	6	5	127	115
2	8	5	67	44
2	10	5	177	170
2	12	5	137	112
2	14	5	91	96
H= 3, L= 5				
3	3	5	-181	-178
3	7	5	-268	-232

H	K	L	FO	K*FC
3	9	5	-67	-64
3	11	5	-171	-167
H= 4, L= 5				
4	6	5	218	211
4	8	5	128	118
4	14	5	104	107
H= 0, L= 6				
0	0	6	-389	-439
0	4	6	-231	-230
0	8	6	-243	-227
0	10	6	158	148
0	14	6	158	196
H= 1, L= 6				
1	1	6	92	103
1	3	6	198	189
1	5	6	135	128
1	9	6	-99	-89
H= 2, L= 6				
2	0	6	-330	-356
2	4	6	-189	-198
2	8	6	-183	-183
2	10	6	137	128
2	14	6	140	160
H= 3, L= 6				
3	3	6	161	145
3	5	6	115	98
H= 4, L= 6				
4	0	6	-211	-250
4	4	6	-111	-131
4	6	6	64	55
4	8	6	-139	-129
H= 0, L= 7				
0	2	7	-141	-118
0	4	7	-100	-110
0	6	7	-100	-98
0	10	7	-163	-156
H= 1, L= 7				
1	3	7	180	206
1	7	7	156	190
1	9	7	68	66
1	11	7	178	194
H= 2, L= 7				
2	2	7	98	91
2	6	7	-271	-238
2	8	7	-133	-136
H= 3, L= 7				
3	3	7	200	210
3	11	7	179	197
H= 4, L= 7				
4	6	7	-84	-72
H= 0, L= 8				
0	0	8	215	242
0	4	8	199	211
H= 1, L= 8				
1	3	8	-136	-133
H= 2, L= 8				
2	0	8	262	295
2	8	8	142	159
H= 3, L= 8				
3	3	8	-121	-119
H= 4, L= 8				

TABLE A3.10

F(OBS), F(CALC) FOR $\text{Cs}_2[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl}_3$ (UNOBSERVED REFLECTIONS MARKED *)

H= 0, L= -6	J	H= 3, L= -6	J	H= 5, L= 0	J
U 2 -6 -188 -148		1 -6 -156 -137		1 0 -459 -433	
H= 0, L= -4	J	H= 3, L= -4	J	3 0 -230 -289	
0 0 -4 317 327		1 -4 306 281		H= 5, L= 2	
0 2 -4 299 259		3 -4 254 229		1 2 283 297	
H= 0, L= -3	J	H= 3, L= -3	J	3 2 227 236	
0 0 -3 -123 -115		1 -3 166 154		H= 5, L= 3	
H= 0, L= -2	J	3 -3 166 148		1 3 156 151	
0 0 -2 -357 -367		H= 3, L= -2	J	3 3 83 95	
0 2 -2 -221 -206		1 -2 -379 -362		H= 5, L= 4	
H= 0, L= -1	J	3 -2 -275 -248		1 4 -200 -168	
0 0 -1 108 136		H= 3, L= -1	J	3 4 -175 -146	
H= 1, L= -6	J	1 -1 -116 -94		H= 5, L= 6	
1 1 -6 140 134		3 -1 -105 -116		1 6 159 162	
H= 1, L= -5	J	H= 3, L= 0	J	3 6 156 158	
1 1 -5 213 192		1 0 292 306		H= 6, L= -6	
1 3 -5 152 135		3 0 168 193		2 -6 -97 -94	
H= 1, L= -4	J	H= 3, L= 1	J	H= 6, L= -5	
1 1 -4 -157 -136		1 1 222 263		0 -5 -143 -161	
1 3 -4 -136 -106		3 1 205 215		6 2 -5 -144 -131	
H= 1, L= -3	J	H= 3, L= 2	J	H= 6, L= -4	
1 1 -3 -166 -167		1 2 -189 -191		0 -4 -192 177	
1 3 -3 -140 -103		3 2 -114 -110		6 2 -4 213 222	
H= 1, L= -2	J	H= 3, L= 4	J	H= 6, L= -3	
1 1 -2 82 80		1 4 224 226		0 -3 277 263	
1 3 -2 106 90		3 4 186 157		6 2 -3 262 253	
H= 1, L= -1	J	H= 3, L= 5	J	H= 6, L= -2	
1 1 -1 329 336		1 5 161 155		0 -2 116 99	
1 3 -1 170 212		3 5 146 119		H= 6, L= -1	
H= 1, L= 1	J	H= 3, L= 6	J	0 -1 -127 -124	
1 1 1 -41 -30		1 6 -155 -155		6 2 -1 -176 -193	
H= 1, L= 2	J	3 6 -143 -117		H= 6, L= 0	
1 1 2 106 143		H= 4, L= -7	J	0 0 177 136	
1 3 2 127 137		2 -7 -144 -126		6 2 0 144 169	
H= 1, L= 3	J	H= 4, L= -5	J	H= 6, L= 1	
1 1 3 235 248		0 -5 209 233		0 1 103 88	
1 3 3 225 204		4 2 -5 221 193		6 2 1 167 186	
H= 1, L= 5	J	H= 4, L= -4	J	H= 6, L= 2	
1 1 5 -132 -133		0 -4 178 160		0 2 -50 -54	
1 3 5 -130 -123		4 2 -4 252 196		H= 6, L= 3	
H= 2, L= -7	J	H= 4, L= -3	J	0 3 -167 -140	
2 2 -7 141 132		0 -3 -167 -191		6 2 3 -156 -186	
H= 2, L= -6	J	2 -3 -127 -99		H= 6, L= 4	
2 2 -6 243 216		H= 4, L= -2	J	0 4 157 145	
H= 2, L= -5	J	2 -2 -67 -43		6 2 4 94 106	
2 2 -5 -111 -89		H= 4, L= -1	J	H= 6, L= 5	
H= 2, L= -4	J	0 -1 214 217		0 5 141 184	
2 0 -4 -212 -168		4 2 -1 85 73		6 2 5 190 190	
2 2 -4 -166 -134		H= 4, L= 0	J	H= 7, L= -8	
H= 2, L= -3	J	0 0 185 169		1 -8 95 118	
2 2 -3 155 129		4 2 0 117 120		H= 7, L= -6	
H= 2, L= -2	J	H= 4, L= 1	J	1 -6 -165 -172	
2 0 -2 270 309		0 1 -303 -283		H= 7, L= -5	
2 2 -2 285 299		4 2 1 -169 -137		1 -5 112 107	
H= 2, L= -1	J	H= 4, L= 3	J	3 -5 112 96	
2 0 -1 -94 -99		0 3 241 260		H= 7, L= -4	
2 2 -1 -171 -199		4 2 3 184 193		1 -4 202 195	
H= 2, L= 0	J	H= 4, L= 4	J	3 -4 198 172	
2 0 0 -128 -145		0 4 273 251		H= 7, L= -2	
2 2 0 -174 -234		4 2 4 172 174		1 -2 -160 -149	
H= 2, L= 1	J	H= 4, L= 5	J	3 -2 -135 -147	
2 0 1 179 174		2 5 -118 -86		H= 7, L= -1	
2 2 1 170 206		H= 5, L= -8	J	1 -1 222 237	
H= 2, L= 2	J	1 -8 -130 -171		3 -1 149 159	
2 2 2 393 473		H= 5, L= -6	J	H= 7, L= 0	
H= 2, L= 4	J	1 -6 216 207		1 0 261 276	
2 0 4 -180 -154		H= 5, L= -5	J	3 0 229 232	
2 2 4 -179 -195		1 -5 64 59		H= 7, L= 2	
H= 2, L= 6	J	H= 5, L= -4	J	1 2 -245 -268	
2 2 6 203 183		1 -4 -210 -217		3 2 -225 -214	
H= 3, L= -8	J	3 -4 -171 -145		H= 7, L= 3	
3 1 -8 107 128		H= 5, L= -3	J	1 3 87 77	
H= 3, L= -7	J	1 -3 138 132		H= 7, L= 4	
3 1 -7 96 87		3 -3 139 109		1 4 198 197	
H= 3, L= -2	J	H= 5, L= -2	J	3 4 178 154	
3 1 -2 418 398		1 -2 303 263		H= 7, L= 6	
H= 3, L= -1	J	H= 5, L= -1	J	1 6 -107 -107	
3 1 -1 103 105		1 -1 103 105			

TABLE A3-10 (cont.)

F(OBS), F(CALC) FOR $\text{CS}_2[\text{VCl}_2(\text{H}_2\text{O})_2]\text{Cl}_3$ (UNOBSERVED REFLECTIONS MARKED *)

8	H= 8, L= -6		11	H= 11, L= -6		14	H= 14, L= 4
2	0 -6 241 194		11	1 -6 121 126		0	4 134 130
	H= 8, L= -4		11	3 -6 123 109			H= 15, L= -6
8	0 -4 -232 -242			H= 11, L= -5		15	1 -6 110 142
8	2 -4 -196 -173		11	1 -5 185 203		15	3 -6 101 123
	H= 8, L= -3		11	3 -5 182 175			H= 15, L= -4
8	0 -3 -74 -91			H= 11, L= -4		15	1 -4 -140 -155
8	2 -3 -128 -118		11	1 -4 -92 -85		15	3 -4 -109 -137
	H= 8, L= -2			H= 11, L= -3		15	H= 15, L= -2
8	0 -2 450 466		11	1 -3 -136 -136		15	1 -2 274 241
8	2 -2 307 316		11	3 -3 -108 -131		15	3 -2 201 205
	H= 8, L= -1			H= 11, L= -1		15	H= 15, L= -1
8	0 -1 292 250		11	1 -1 219 205		15	1 -1 120 99
8	2 -1 202 212			H= 11, L= 2		15	3 -1 92 87
	H= 8, L= 0		11	1 2 116 108			H= 15, L= 0
8	0 0 -213 -183			H= 11, L= 3		15	1 0 -232 -203
8	2 0 -97 -79		11	1 3 196 207		15	3 0 -128 -170
	H= 8, L= 1		11	3 3 128 165			H= 15, L= 2
8	0 1 -195 -171			H= 12, L= -6		15	1 2 135 148
8	2 1 -91 -107		12	2 -6 252 212		15	3 2 80 121
	H= 8, L= 2			H= 12, L= -4		15	H= 15, L= 3
8	0 2 260 270		12	2 -4 -95 -105		15	1 3 86 86
8	2 2 203 199			H= 12, L= -2		16	H= 16, L= -5
	H= 8, L= 3		12	0 -2 245 223		16	2 -5 -125 -146
8	0 3 128 137		12	2 -2 197 203			H= 16, L= -4
8	2 3 92 79			H= 12, L= -1		16	2 -4 94 91
	H= 8, L= 4		12	0 -1 -144 -131		16	H= 16, L= -3
8	0 4 -140 -139			H= 12, L= 0		16	2 -3 161 172
8	2 4 -118 -123		12	0 0 -229 -184			H= 16, L= -1
	H= 8, L= 6		12	2 0 -142 -142		16	0 -1 -100 -120
8	2 6 139 161			H= 12, L= 1			H= 16, L= 0
	H= 9, L= -7		12	0 1 114 96		16	0 0 122 112
9	1 -7 157 178		12	2 1 93 55		16	2 0 116 79
	H= 9, L= -5			H= 12, L= 2			H= 16, L= 1
9	1 -5 -116 -123		12	0 2 257 302		16	0 1 138 140
	H= 9, L= -4		12	2 2 240 241			H= 16, L= 3
9	1 -4 -106 -93			H= 12, L= 4		16	0 3 -125 -148
9	3 -4 -62 -65		12	0 4 -115 -116			H= 17, L= -6
	H= 9, L= -3			H= 13, L= -6		17	1 -6 -96 -123
9	1 -3 175 195		13	1 -6 -118 -138			H= 17, L= -4
9	3 -3 137 135		13	3 -6 -81 -102		17	1 -4 117 118
	H= 9, L= -2			H= 13, L= -4			H= 17, L= -2
9	1 -2 121 105		13	1 -4 217 234		17	1 -2 -98 -112
	H= 9, L= 1		13	3 -4 182 175			H= 17, L= -1
9	1 1 251 246			H= 13, L= -3		17	1 -1 138 111
9	3 1 183 197		13	1 -3 192 189			H= 17, L= 0
	H= 9, L= 2		13	3 -3 130 137		17	1 0 190 176
9	1 2 136 108			H= 13, L= -2		17	3 0 128 135
	H= 9, L= 3		13	1 -2 -231 -196			H= 17, L= 2
9	1 3 -95 -96		13	3 -2 -144 -149		17	1 2 -115 -144
	H= 9, L= 4			H= 13, L= -1			H= 18, L= -4
9	1 4 -122 -114		13	1 -1 -144 -124		18	2 -4 -133 -134
	H= 9, L= 5		13	3 -1 -91 -83			H= 18, L= -3
9	1 5 94 104			H= 13, L= 0		18	2 -3 -108 -106
	H= 9, L= 6		13	1 0 185 145			H= 18, L= -2
9	3 6 72 70		13	3 0 112 118		18	2 -2 196 183
	H= 10, L= -6			H= 13, L= 1			H= 18, L= -1
10	2 -6 -118 -117		13	1 1 191 172		18	0 -1 135 161
	H= 10, L= -4			H= 13, L= 2			
10	0 -4 219 277		13	1 2 -99 -112			
10	2 -4 272 255			H= 13, L= 4			
	H= 10, L= -2		14	1 4 86 140			
10	0 -2 -222 -230			H= 14, L= -5			
10	2 -2 -273 -248		14	2 -5 134 143			
	H= 10, L= 0			H= 14, L= -4			
10	0 0 387 372		14	2 -4 137 115			
10	2 0 382 393			H= 14, L= -1			
	H= 10, L= 1		14	0 -1 95 102			
10	0 1 164 133		14	2 -1 134 131			
10	2 1 134 113			H= 14, L= 0			
	H= 10, L= 2		14	0 0 69 91			
10	0 2 -179 -129		14	2 0 118 76			
10	2 2 -153 -167			H= 14, L= 1			
	H= 10, L= 4		14	0 1 -157 -124			
10	0 4 202 194			H= 14, L= 3			
10	2 4 164 198		14	0 3 133 115			

TABLE A3.11

F(OBS), F(CALC) FOR $\text{Cs}_2(\text{VBr}_2(\text{H}_2\text{O})_2)_2$ (UNOBSERVED REFLECTIONS MARKED*)

H	K	L	F _O	K+F _C	H	K	L	F _O	K+F _C	H	K	L	F _O	K+F _C		
		H=-23, L= 3					H= 13, L= 3					H= 2, L= 1	-163	-115		
-23	1	3	141	228	13	3	3	68	46	8	4	1	-137	-119		
		H=-23, L= 4					H= 13, L= 4					H= 0, L= 2	361	414		
-23	1	4	101	183	13	3	4	194	222	8	2	2	313	319		
		H=-22, L= 0					H= 13, L= 5					8	2	203	207	
-22	0	0	-86	-116	13	3	5	126	163	8	2	3	-69	-73		
		H=-22, L= 1					H= 14, L= 1					H= 8, L= 4	-267	-234		
-22	2	1	-55	-69	14	0	1	-181	-184	8	0	4	-190	-222		
		H=-22, L= 2					H= 14, L= 2					8	4	-134	-126	
-22	0	2	122	167	14	2	1	-162	-209	8	2	4	-134	-126		
-22	2	2	94	149	14	4	1	-116	-105	8	4	4	-134	-126		
		H=-22, L= 3					H= 14, L= 3					H= 0, L= 5	-141	-137		
-22	0	3	78	53	14	0	3	96	91	8	0	5	-116	-82		
		H=-21, L= 1					H= 14, L= 4					H= 8, L= 6	296	369		
-21	3	1	76	92	14	2	3	91	91	8	2	6	171	175		
		H=-21, L= 3					H= 14, L= 4					H= 8, L= 7	108	127		
-21	1	3	174	242	14	4	4	184	211	8	4	7	296	297		
		H=-21, L= 6					H= 15, L= 1					H= 9, L= 1	296	297		
-21	1	6	135	127	15	3	1	-111	-114	9	3	1	-91	-74		
		H=-20, L= 0					H= 15, L= 2					H= 9, L= 3	-214	-206		
-20	0	0	262	314	15	3	2	121	128	9	3	3	84	83		
-20	2	0	186	231	15	3	3	119	137	9	3	3	84	83		
		H=-20, L= 1					H= 15, L= 3					H= 9, L= 5	91	89		
-20	0	1	-130	-158	15	3	4	-132	-131	9	3	4	336	362		
-20	2	1	-120	-151	15	3	4	-132	-131	9	3	4	336	362		
-20	4	1	-67	-85	15	3	4	-132	-131	9	3	4	336	362		
		H=-20, L= 2					H= 16, L= 0					H= 10, L= 0	257	233		
-20	0	2	-226	-250	16	0	0	137	135	10	0	0	257	233		
-20	2	2	-181	-186	16	2	2	-109	-103	10	2	1	262	224		
-20	4	2	-114	-135	16	4	2	-64	-55	10	4	1	153	121		
		H=-20, L= 4					H= 16, L= 2					H= 10, L= 1	257	233		
-20	0	4	223	282	16	2	3	-111	-152	10	0	1	257	233		
-20	2	4	203	239	16	4	3	-79	-116	10	2	1	262	224		
-20	4	4	100	156	16	4	3	-79	-116	10	4	1	153	121		
		H=-19, L= 4					H= 16, L= 4					H= 10, L= 2	-212	-144		
-19	1	4	-90	-85	16	2	4	111	122	10	0	2	-212	-144		
		H=-19, L= 7					H= 17, L= 2					10	2	2	-207	-167
-19	1	7	164	185	17	3	2	-160	-206	10	4	2	-130	-84		
		H=-18, L= 1					H=-14, L= 2					H=-11, L= 5	301	317		
-18	0	1	181	201	14	0	2	156	109	11	1	5	301	317		
-18	2	1	196	182	14	2	2	177	123	11	3	5	238	288		
-18	4	1	85	112	14	4	2	86	57							
		H=-18, L= 2					H=-14, L= 4					H=-11, L= 6	247	238		
-18	0	2	320	289	14	0	4	343	288	11	1	6	247	238		
-18	2	2	245	294	14	0	4	343	288	11	3	6	201	216		
-18	4	2	150	160	14	2	4	211	186							
		H=-18, L= 3					H=-14, L= 4					H=-11, L= 8	-174	-143		
-18	0	3	-245	-267	14	4	4	187	149	11	1	8	-174	-143		
-18	2	3	-175	-204	14	2	7	-225	-201	11	3	8	-128	-133		
-18	4	3	-98	-142	14	4	7	-158	-146	11	3	8	-128	-133		
		H=-18, L= 4					H=-14, L= 7					H=-10, L= 0	623	697		
-18	0	4	-232	-231	14	0	7	-225	-201	10	0	0	623	697		
-18	2	4	-212	-226	14	2	7	-158	-146	10	2	0	579	686		
-18	4	4	-121	-126	14	4	7	-84	-110							
		H=-18, L= 6					H=-13, L= -2					H=-10, L= 1	-192	-160		
-18	0	6	225	295	13	1	-2	-194	-216	10	0	1	-192	-160		
-18	2	6	207	252	13	1	-2	-194	-216	10	2	1	-130	-90		
		H=-17, L= 0					H=-13, L= -1					10	4	1	-78	-76
-17	1	0	243	244	13	1	-1	208	210							
-17	3	0	171	205	13	1	-1	208	210							
		H=-17, L= 1					H=-13, L= 0					H=-10, L= 2	-496	-401		
-17	1	1	210	174	13	1	0	227	144	10	0	2	-496	-401		
-17	3	1	141	159	13	3	0	167	134	10	2	2	-451	-413		
		H=-17, L= 2					H=-13, L= 1					10	4	2	-248	-213
-17	1	2	-157	-143	13	1	1	-233	-174	10	4	2	-248	-213		
-17	3	2	-110	-111	13	3	1	-142	-130	10	4	2	-248	-213		
		H=-17, L= 3					H=-13, L= 2					H=-10, L= 3	-244	-141		
-17	1	3	-157	-143	13	1	2	-488	-384	10	2	3	-244	-141		
-17	3	3	-110	-111	13	3	2	-323	-323	10	4	3	-244	-141		
		H=-17, L= 6					H=-13, L= 3					H=-10, L= 4	443	431		
-17	1	6	-200	-176	13	1	3	418	338	10	0	4	443	431		
-17	3	6	-133	-153	13	3	3	273	272	10	2	4	347	371		
		H=-17, L= 7					H=-13, L= 4					10	4	4	211	225
-17	1	7	118	73	13	1	4	406	404	10	4	4	211	225		
-17	3	7	79	71	13	3	4	294	333	10	4	4	211	225		
		H=-16, L= 0					H=-13, L= 6					H=-10, L= 5	-94	-108		
-16	0	0	283	259	13	1	6	-242	-260	10	0	5	-94	-108		
-16	2	0	205	199	13	3	6	-192	-212	10	2	5	-94	-108		
		H=-16, L= 2					H=-13, L= 7					H=-10, L= 6	-100	-132		
-16	0	2	70	44	13	1	7	90	99	10	0	6	-100	-132		
		H=-16, L= 2					H=-13, L= 8					H=-10, L= 7	147	133		
-16	0	2	70	44	13	1	8	112	103	10	0	7	147	133		
		H=-16, L= 2					H=-13, L= 8					10	2	7	128	87
-16	0	2	70	44	13	3	8	74	85	10	2	8	128	87		
		H=-16, L= 2					H=-13, L= 8					H=-10, L= 8	437	357		
-16	0	2	70	44	13	3	8	74	85	10	4	8	437	357		
		H=-16, L= 2					H=-13, L= 8					10	2	8	292	269
-16	0	2	70	44	13	3	8	74	85	10	4	8	292	269		
		H=-16, L= 2					H=-13, L= 8					H=-10, L= 9	-64	-45		
-16	0	2	70	44	13	3	8	74	85	10	0	9	-64	-45		
		H=-16, L= 2					H=-13, L= 8					H= -9, L= -4	-140	-237		
-16	0	2	70	44	13	3	8	74	85	9	1	-4	-140	-237		

TABLE A3.11 (CONT.)

F(OBS), F(CALC) FOR $\text{Cs}_2[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br}_3$ (UNOBSERVED REFLECTIONS MARKED*)

H	K	L	F _O	K+F _C	H	K	L	F _O	K+F _C	H	K	L	F _O	K+F _C	H	K	L	F _O	K+F _C
3	3	4	281	267	-1	1	4	-416	-323	-3	1	-4	342	342	-6	0	3	320	298
3	3	5	175	106	-1	3	4	-237	-265	-3	1	-3	219	203	-6	2	3	281	267
3	3	6	-317	-264	-1	1	5	328	235	-3	1	-2	-244	-240	-6	4	3	169	152
4	0	1	-305	-349	-1	3	5	224	164	-3	1	-1	310	364	-6	0	4	331	362
4	2	1	-219	-150	-1	3	6	215	164	-3	1	-2	-244	-240	-6	2	4	310	402
4	4	1	-182	-153	-1	3	7	132	92	-3	1	0	361	375	-6	4	4	187	192
4	2	2	156	130	-1	3	8	-118	-67	-3	3	0	363	261	-6	0	5	-221	-172
4	0	3	276	264	0	0	1	129	200	-3	1	1	-193	-139	-6	2	6	-150	-170
4	2	3	224	199	0	2	1	75	85	-3	1	2	-520	-725	-6	4	6	-136	-131
4	4	3	154	133	0	4	1	44	75	-3	3	2	-401	-567	-6	0	8	300	144
4	0	4	528	486	0	0	2	-395	-555	-3	1	3	219	222	-6	2	8	211	163
4	2	4	342	321	0	2	2	-258	-314	-3	3	3	192	210	-6	4	8	119	106
4	4	4	255	242	0	4	2	-244	-241	-3	3	4	323	412	-6	0	9	-58	-50
4	0	6	-167	-122	0	0	3	-343	-308	-3	1	4	491	474	-6	1	-4	-320	-254
4	2	6	-95	-71	0	2	3	-135	-131	-3	3	5	306	204	-6	1	-3	266	301
4	2	8	114	89	0	4	3	-161	-135	-3	3	6	175	162	-6	1	-2	357	410
5	3	2	315	355	0	0	4	532	463	-3	1	6	-326	-228	-6	1	-1	-127	-96
5	3	3	241	236	0	2	4	378	370	-3	3	6	-256	-212	-6	3	0	-676	-653
5	3	4	-262	-237	0	4	4	255	232	-3	1	7	136	116	-6	1	1	265	181
5	3	5	155	112	0	0	6	-260	-179	-3	3	7	121	100	-6	1	2	604	621
5	3	6	265	230	0	2	6	-247	-186	-3	3	8	141	121	-6	3	2	494	467
5	3	7	64	57	0	4	6	-130	-100	-3	3	8	141	121	-6	1	3	361	299
-8	4	6	174	196	0	0	8	440	352	-2	0	0	-228	-196	-6	3	3	292	255
-8	0	9	95	93	0	2	8	386	336	-2	0	1	-206	-190	-6	1	1	219	216
-8	2	9	56	95	1	3	1	207	214	-2	2	1	-368	-307	-6	3	3	238	218
-7	1	-5	140	176	-5	1	4	-312	-333	-2	4	1	-108	-105	-6	1	4	-359	-231
-7	1	-4	248	266	-5	3	4	-221	-253	-2	0	2	293	440	-6	3	5	-152	-120
-7	1	-2	-452	-559	-5	1	5	211	166	-2	2	2	294	386	-6	1	7	215	178
-7	1	0	443	397	-5	3	5	126	144	-2	4	2	159	203	-6	3	8	-148	-117
-7	3	0	407	340	-5	1	6	305	231	-2	0	3	-178	-211	-6	1	9	-140	-114
-7	1	1	460	370	-5	3	6	207	186	-2	2	4	-281	-240	-6	3	9	-156	-146
-7	3	1	408	279	-5	1	8	-283	-296	-2	4	4	-120	-117	-6	1	10	-140	-114
-7	3	2	-307	-204	-5	3	8	-239	-254	-2	4	4	-120	-117	-6	3	11	-140	-114
-7	1	3	295	205	-4	2	0	184	99	-2	0	6	597	523	-6	1	12	-140	-114
-7	3	3	224	158	-4	2	1	-311	-188	-2	2	6	388	384	-6	3	13	-140	-114
-7	1	4	237	206	-4	2	2	-311	-188	-2	4	6	262	272	-6	1	14	-140	-114
-7	3	4	193	194	-4	0	2	51	46	-2	0	7	125	106	-6	3	15	-140	-114
-7	1	6	-380	-342	-4	0	3	-122	-109	-2	2	7	114	92	-6	1	16	-140	-114
-7	3	6	-276	-299	-4	0	4	355	362	-2	0	8	-140	-125	-6	3	17	-140	-114
-7	1	8	197	172	-4	2	4	291	398	-2	2	8	-113	-72	-6	1	18	-140	-114
-7	3	8	154	147	-4	4	4	167	191	-2	0	9	-117	-132	-6	3	19	-140	-114
-6	0	0	323	270	-4	0	5	251	207	-1	1	-5	-153	-114	-6	1	20	-140	-114
-6	2	0	334	267	-4	2	5	174	169	-1	1	-4	-291	-263	-6	3	21	-140	-114
-6	2	1	-286	-176	-4	4	5	105	111	-1	1	-3	-264	-236	-6	1	22	-140	-114
-6	4	1	-98	-53	-4	0	6	144	111	-1	1	-2	183	234	-6	3	23	-140	-114
-6	0	2	311	241	-4	0	7	-280	-163	-1	1	-1	178	317	-6	1	24	-140	-114
-6	4	2	164	94	-4	2	7	-186	-169	-1	1	1	761	377	-6	3	25	-140	-114
					-4	4	7	-88	-93	-1	3	1	191	263	-6	1	26	-140	-114
					-4	0	8	-172	-337	-1	1	3	-196	-164	-6	3	27	-140	-114
					-4	2	8	158	140	-1	3	3	-147	-108	-6	1	28	-140	-114

[illegible]

TABLE A3.12

F(OBS), F(CALC) FOR $\text{Rb}[\text{VCl}_2(\text{H}_2\text{O})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (UNOBSERVED REFLECTIONS MARKED*)

H	K	L	F(O)	K*F(C)	H	K	L	F(O)	K*F(C)	H	K	L	F(O)	K*F(C)
H= 2, K= 0					1	9	3	80	54	H= 4, K= 4				
2	0	0	-113	-117	1	9	4	115	125	4	4	0	352	312
2	0	2	-438	-390	H= 3, K= 9					4	4	2	-82	-63
2	0	4	-115	-57	3	9	2	-244	-254	4	4	4	216	226
H= 4, K= 0					H= 5, K= 9					H= 6, K= 4				
4	0	0	324	308	5	9	0	158	167	6	4	0	-82	-67
4	0	2	-173	-143	5	9	1	-131	-160	6	4	1	-101	-101
4	0	4	210	210	5	9	4	130	137	6	4	2	-306	-291
H= 6, K= 0					H= 0, K= 10					H= 5, K= 4				
6	0	0	-157	-136	0	10	2	-133	-123	5	4	0	153	159
6	0	4	100	67	H= 2, K= 10					5	4	4	113	129
H= 8, K= 0					2	10	0	121	129	H= 1, K= 5				
8	0	4	113	92	2	10	1	121	133	1	5	0	97	87
H= 1, K= 1					2	10	2	-197	-174	1	5	1	-232	-241
1	1	0	224	230	2	10	4	124	98	1	5	2	-297	-288
1	1	1	-155	-158	H= 4, K= 10					1	5	3	-207	-200
1	1	2	-133	-196	4	10	0	92	67	1	5	4	58	70
1	1	3	-116	-123	H= 6, K= 10					H= 3, K= 5				
1	1	4	158	160	6	10	0	94	118	3	5	0	323	313
H= 3, K= 1					6	10	4	92	93	3	5	1	63	70
3	1	0	-74	-61	H= 1, K= 11					3	5	2	45	11
3	1	1	192	197	1	11	0	89	88	3	5	4	205	228
3	1	2	-466	-467	1	11	2	-153	-150	H= 5, K= 5				
3	1	3	178	163	H= 3, K= 11					5	5	2	-267	-266
H= 5, K= 1					3	11	0	114	134	H= 7, K= 5				
5	1	0	249	239	3	11	4	130	111	7	5	0	157	135
5	1	1	-269	-244	H= 5, K= 11					7	5	2	-66	-79
5	1	2	-70	-50	5	11	0	140	123	7	5	4	124	110
5	1	3	-216	-216	H= 0, K= 12					H= 2, K= 6				
5	1	4	172	180	0	12	0	133	136	2	6	0	287	305
H= 7, K= 1					0	12	2	-149	-124	2	6	1	-63	-80
7	1	0	106	113	0	12	4	92	102	2	6	2	-90	-112
7	1	1	87	95	H= 2, K= 12					2	6	3	-80	-72
7	1	2	-149	-130	2	12	2	-151	-131	2	6	4	254	224
7	1	4	86	90	H= 4, K= 12					H= 4, K= 6				
H= 9, K= 1					4	12	0	183	210	4	6	0	-52	-62
9	1	0	70	106	4	12	4	169	171	4	6	2	-294	-295
H= 0, K= 2					H= 1, K= 13					H= 6, K= 6				
0	2	2	-248	-261	1	13	1	-196	-195	6	6	0	245	233
H= 2, K= 2					1	13	2	-154	-172	6	6	1	139	108
2	2	0	308	312	1	13	3	-192	-186	H= 0, K= 14				
2	2	1	85	73	6	6	4	152	180	0	14	2	-139	-138
2	2	2	-247	-237	H= 8, K= 6					H= 2, K= 14				
2	2	3	95	61	8	6	1	-121	-125	2	14	0	158	179
2	2	4	178	211	H= 1, K= 7					H= 4, K= 14				
H= 4, K= 2					1	7	0	266	278	4	14	2	-162	-175
4	2	2	-243	-194	1	7	1	195	178	H= 6, K= 14				
4	2	3	-45	-15	1	7	2	-67	-21					
4	2	4	46	42	1	7	3	156	151					
H= 6, K= 2					1	7	4	178	196					
6	2	0	243	227	H= 3, K= 7									
6	2	1	-188	-178	3	7	0	89	100					
6	2	2	-98	-102	3	7	1	-174	-174					
6	2	4	165	170	3	7	2	-210	-200					
H= 8, K= 2					3	7	3	-151	-155					
8	2	1	134	157	H= 5, K= 7									
H= 1, K= 3					5	7	0	103	92					
1	3	0	110	109	5	7	1	170	177					
1	3	1	129	111	5	7	2	-171	-162					
1	3	2	-250	-305	5	7	4	87	76					
1	3	3	62	89	H= 7, K= 7									
1	3	4	104	84	7	7	0	137	145					
H= 3, K= 3					7	7	4	113	125					
3	3	0	308	312	H= 0, K= 8									
3	3	1	153	144	0	8	0	381	386					
3	3	3	91	114	0	8	2	-72	-38					
3	3	4	197	219	0	8	4	325	287					
H= 5, K= 3					H= 2, K= 8									
5	3	0	101	86	2	8	0	-52	-62					
5	3	2	-239	-218	2	8	1	74	74					
5	3	4	76	70	2	8	2	-288	-295					
H= 7, K= 3					H= 4, K= 8									
7	3	2	-179	-178	4	8	0	146	153					
H= 9, K= 3					4	8	1	-118	-111					
9	3	0	71	104	4	8	2	-164	-165					
9	3	1	122	124	4	8	4	122	114					
H= 0, K= 4					H= 6, K= 8									
0	4	0	147	97	6	8	0	94	90					
0	4	2	-454	-464	6	8	2	-67	-76					
0	4	4	120	75	H= 8, K= 8									
H= 2, K= 4					8	8	0	141	132					
2	4	0	196	193	H= 1, K= 9									
2	4	1	-137	-139	1	9	0	136	154					
2	4	3	-78	-111	1	9	2	-134	-112					
2	4	4	136	138										

TABLE A3.13

F(OBS), F(CALC) FOR $[VBr_2(H_2O)_4]Br \cdot 2H_2O$ (UNOBSERVED REFLECTIONS MARKED*)

h	k	l	F(O)	F(C)	h	k	l	F(O)	F(C)	h	k	l	F(O)	F(C)
K = 0, L = -14														
4	0	-14	274	331										
K = 0, L = -12														
1	0	-12	-140	-202										
3	0	-12	133	193										
4	0	-12	207	314										
5	0	-12	-141	-203										
6	0	-12	120	165										
K = 0, L = -10														
1	0	-10	-100	-125										
2	0	-10	211	265										
6	0	-10	423	469										
K = 0, L = -8														
1	0	-8	341	317										
2	0	-8	391	335										
3	0	-8	-407	-429										
4	0	-8	461	444										
6	0	-8	53	46										
K = 0, L = -6														
1	0	-6	-350	-204										
3	0	-6	190	106										
4	0	-6	401	447										
5	0	-6	-446	-406										
6	0	-6	271	221										
7	0	-6	170	220										
K = 0, L = -4														
1	0	-4	-402	-270										
2	0	-4	824	829										
3	0	-4	73	106										
5	0	-4	-69	-86										
6	0	-4	515	453										
7	0	-4	-180	-106										
8	0	-4	61	55										
K = 0, L = -2														
1	0	-2	570	612										
2	0	-2	558	622										
3	0	-2	-454	-672										
4	0	-2	505	501										
5	0	-2	141	191										
7	0	-2	-186	-195										
8	0	-2	247	320										
K = 0, L = 0														
2	0	0	-256	-201										
4	0	0	432	741										
5	0	0	-377	-305										
6	0	0	181	159										
7	0	0	87	125										
K = 0, L = 2														
0	0	2	396	373										
1	0	2	-605	-552										
2	0	2	1177	1272										
3	0	2	345	293										
5	0	2	-181	-140										
6	0	2	555	521										
7	0	2	-101	-90										
K = 0, L = 4														
0	0	4	91	100										
1	0	4	789	735										
2	0	4	850	889										
3	0	4	-602	-526										
4	0	4	307	352										
5	0	4	299	247										
6	0	4	165	149										
7	0	4	-164	-145										
K = 0, L = 6														
0	0	6	936	907										
1	0	6	-286	-266										
2	0	6	-138	-89										
3	0	6	260	202										
4	0	6	686	711										
5	0	6	-242	-229										
7	0	6	142	124										
K = 0, L = 8														
0	0	8	84	135										
1	0	8	-542	-576										
2	0	8	567	572										
3	0	8	241	205										
5	0	8	-111	-115										
6	0	8	421	365										
K = 0, L = 10														
1	0	10	214	191										
2	0	10	358	308										
3	0	10	-453	-405										
4	0	10	154	202										
5	0	10	278	208										
K = 0, L = 12														
0	0	12	497	497										
4	0	12	373	319										
K = 0, L = 14														
0	0	14	138	105										
2	0	14	234	279										
K = 1, L = -12														
K = 1, L = -10														
1	1	-10	257	306										
K = 1, L = -13														
1	1	-13	342	374										
2	1	-13	-312	-344										
3	1	-13	175	195										
5	1	-13	100	147										
K = 1, L = -11														
3	1	-11	611	597										
K = 1, L = -9														
1	1	-9	671	734										
2	1	-9	257	321										
4	1	-9	-322	-312										
5	1	-9	492	540										
K = 1, L = -8														
3	1	-8	-145	-124										
4	1	-8	-68	-102										
K = 1, L = -7														
1	1	-7	495	441										
2	1	-7	-629	-611										
3	1	-7	559	292										
4	1	-7	361	355										
5	1	-7	311	272										
6	1	-7	-304	-317										
7	1	-7	267	313										
K = 1, L = -6														
1	1	-6	263	222										
2	1	-6	-75	-43										
3	1	-6	-200	-153										
4	1	-6	-66	-35										
K = 1, L = -5														
1	1	-5	-223	-171										
2	1	-5	97	75										
3	1	-5	1285	1190										
4	1	-5	-319	-292										
7	1	-5	396	387										
K = 1, L = -4														
1	1	-4	135	97										
2	1	-4	197	147										
3	1	-4	126	156										
5	1	-4	-159	-141										
K = 1, L = -3														
1	1	-3	951	950										
2	1	-3	456	436										
3	1	-3	118	81										
4	1	-3	-436	-393										
5	1	-3	786	799										
K = 1, L = -2														
1	1	-2	103	74										
2	1	-2	403	327										
3	1	-2	235	165										
K = 1, L = -1														
2	1	-1	-456	-949										
3	1	-1	413	345										
4	1	-1	519	554										
5	1	-1	471	429										
6	1	-1	-459	-443										
7	1	-1	336	298										
K = 1, L = 0														
3	1	0	104	88										
4	1	0	188	219										
5	1	0	95	96										
K = 1, L = 1														
1	1	1	246	167										
2	1	1	-161	-156										
3	1	1	939	1060										
4	1	1	-346	-334										
6	1	1	231	196										
7	1	1	506	444										
8	1	1	-200	-199										
K = 1, L = 2														
0	1	2	120	106										
1	1	2	-128	-121										
2	1	2	-132	-135										
3	1	2	71	91										
4	1	2	65	112										
K = 1, L = 3														
0	1	3	-477	-452										
1	1	3	744	790										
2	1	3	494	470										
3	1	3	123	155										
4	1	3	-214	-269										
5	1	3	665	681										
8	1	3	96	103										
K = 1, L = 4														
0	1	4	-180	-153										
1	1	4	-71	-75										
K = 1, L = 5														
0	1	5	-143	-110										
1	1	5	1015	1063										
K = 1, L = 6														
0	1	6	-161	-161										
3	1	6	-99	-113										
K = 1, L = 7														
0	1	7	375	344										
2	1	7	-322	-312										
7	1	7	267	262										
K = 1, L = 8														
0	1	8	-161	-161										
3	1	8	-99	-113										
K = 1, L = 9														
0	1	9	375	344										
2	1	9	-322	-312										
7	1	9	267	262										
K = 1, L = 10														
0	1	10	-161	-161										
3	1	10	-99	-113										
K = 1, L = 11														
0	1	11	375	344										
2	1	11	-322	-312										
7	1	11	267	262										
K = 1, L = 12														
0	1	12	-161	-161										
3	1	12	-99	-113										
K = 1, L = 13														
0	1	13	375	344										
2	1	13	-322	-312										
7	1	13	267	262										
K = 1, L = 14														
0	1	14	-161	-161										
3	1	14	-99	-113										
K = 1, L = 15														
0	1	15	375	344										
2	1	15	-322	-312										
7	1	15	267	262										
K = 1, L = 16														
0	1	16	-161	-161										
3	1	16	-99	-113										
K = 1, L = 17														
0	1	17	375	344										
2	1	17	-322	-312										
7	1	17	267	262										
K = 1, L = 18														
0	1	18	-161	-161										
3	1	18	-99	-113										
K = 1, L = 19														
0	1	19	375	344										
2	1	19	-322	-312										
7	1	19	267	262										
K = 1, L = 20														
0	1	20	-161	-161										
3	1	20	-99	-113										
K = 1, L = 21														
0	1	21	375	344										
2	1	21	-322	-312										
7	1	21	267	262										
K = 1, L = 22														
0	1	22	-161	-161										
3	1	22	-99	-113										
K = 1, L = 23														
0	1	23	375	344										
2	1	23	-322	-312										
7	1	23	267	262										
K = 1, L = 24														
0	1	24	-161	-161										
3	1	24	-99	-113										
K = 1, L = 25														
0	1	25	375	344										
2	1	25	-322	-312										
7	1	25	267	262										
K = 1, L = 26														
0	1	26	-161	-161										
3	1	26	-99	-113										
K = 1, L = 27														
0	1	27	375	344										
2	1	27	-322	-312										
7	1	27	267	262										
K = 1, L = 28														
0	1	28	-161	-161										
3	1	28	-99	-113										
K = 1, L = 29														
0	1	29	375	344										
2	1	29	-322	-312										
7	1	29	267	262										
K = 1, L = 30														
0	1	30	-161	-161										
3	1	30	-99	-113										
K = 1, L = 31														
0	1	31	375	344										
2	1	31	-322	-312										
7	1	31	267	262										
K = 1, L = 32														
0	1	32	-161	-161										
3	1	32	-99	-113										
K = 1, L = 33														
0	1	33	375	344										
2	1	33	-322	-312										
7	1	33	267	262										
K = 1, L = 34														
0	1	34	-161	-161										
3	1	34	-99	-113										
K = 1, L = 35														
0	1	35	375	344										
2	1	35	-322	-312										
7	1	35	267	262										
K = 1, L = 36														
0	1	36	-161	-161										
3	1	36	-99	-113										
K = 1, L = 37														
0	1	37	375	344										
2	1	37	-322	-312										
7	1	37	267	262										
K =														

TABLE A3.13 (CONT.)

F(OBS), F(CALC) FOR $[\text{VBr}_2(\text{H}_2\text{O})_4]\text{Br}\cdot 2\text{H}_2\text{O}$ (UNOBSERVED REFLECTIONS MARKED*)

H	K	L	F _O	F _C	H	K	L	F _O	F _C
0	2	0	275	217					
1	2	0	162	193					
	K=2	L=1			2	3	-2	-110	-76
0	2	1	309	300	3	3	-2	795	764
2	2	1	-415	-369	4	3	-2	-313	-223
4	2	1	175	190	6	3	-2	103	133
					7	3	-2	224	310
	K=2	L=2							
0	2	2	53	75	1	3	-4	-274	-273
1	2	2	-946	-967	3	3	-4	219	227
2	2	2	943	942	5	3	-4	-132	-169
3	2	2	104	190	7	3	-4	113	127
5	2	2	-110	-100					
7	2	2	330	335		K=3	L=-3		
			-90	-74	1	3	-3	766	854
	K=2	L=3			2	3	-3	380	320
0	2	3	166	161	4	3	-3	-485	-416
1	2	3	-158	-144	5	3	-3	684	613
	K=2	L=4				K=3	L=-2		
0	2	4	190	216	1	3	-2	-210	-189
1	2	4	587	516	2	3	-2	175	190
2	2	4	601	604	3	3	-2	-72	-69
3	2	4	-689	-722	4	3	-2	-208	-216
4	2	4	303	313	6	3	-2	135	99
5	2	4	224	231					
6	2	4	125	143		K=3	L=-1		
7	2	4	-160	-167	1	3	-1	887	908
					2	3	-1	-461	-485
	K=2	L=5			3	3	-1	369	343
0	2	5	-109	-134	4	3	-1	589	320
1	2	5	253	255	5	3	-1	301	272
2	2	5	192	204	6	3	-1	-413	-356
3	2	5	-171	-160					
4	2	5	-95	-120		K=3	L=0		
					1	3	0	101	104
	K=2	L=6			2	3	0	-250	-255
0	2	6	990	1149	3	3	0	-295	-226
1	2	6	-149	-145	4	3	0	142	140
2	2	6	-179	-134	6	3	0	-143	-159
4	2	6	580	633					
5	2	6	-291	-274		K=3	L=1		
					1	3	1	42	56
	K=2	L=7			2	3	1	-78	-55
0	2	7	70	62	3	3	1	1086	902
1	2	7	82	97	4	3	1	-210	-204
					6	3	1	76	84
	K=2	L=8			7	3	1	310	352
0	2	8	284	296					
1	2	8	-391	-407		K=3	L=2		
2	2	8	684	698	0	3	2	348	386
3	2	8	227	192	1	3	2	-140	-110
					2	3	2	-220	-205
5	2	8	-143	-172	3	3	2	106	114
6	2	8	432	365	5	3	2	-156	-172
	K=2	L=9				K=3	L=3		
1	2	9	-133	-172	0	3	3	-499	-539
					1	3	3	535	494
	K=2	L=10			2	3	3	272	256
0	2	10	136	148	3	3	3	153	212
1	2	10	247	277	4	3	3	-294	-261
2	2	10	449	447	5	3	3	661	583
3	2	10	-351	-337					
4	2	10	234	227		K=3	L=4		
5	2	10	262	186	2	3	4	193	233
					4	3	4	-187	-196
	K=2	L=12							
0	2	12	432	506		K=3	L=5		
					1	3	5	885	844
	K=2	L=14			2	3	5	-397	-465
0	2	14	173	189	3	3	5	106	174
1	2	14	-194	-205	4	3	5	263	247
					5	3	5	397	327
	K=3	L=-13			6	3	5	-292	-247
1	3	-13	275	353					
						K=3	L=6		
	K=3	L=-11			1	3	6	339	300
3	3	-11	457	523	3	3	6	-90	-101
					6	3	6	-114	-88
	K=3	L=-9							
1	3	-9	475	493		K=3	L=7		
2	3	-9	190	220	0	3	7	215	267
3	3	-9	114	80	1	3	7	118	138
4	3	-9	-157	-193	2	3	7	-217	-213
5	3	-9	374	438	3	3	7	540	566
	K=3	L=-8				K=3	L=8		
2	3	-8	200	205	0	3	8	106	155
4	3	-8	-66	-100	3	3	8	161	150
	K=3	L=-7				K=3	L=9		
1	3	-7	514	566	0	3	9	-371	-457
2	3	-7	-515	-573	1	3	9	278	240
3	3	-7	241	232	2	3	9	295	245
4	3	-7	243	310	3	3	9	212	210
5	3	-7	337	278	4	3	9	-255	-235
6	3	-7	-239	-251	5	3	9	407	301
7	3	-7	167	237					
						K=3	L=10		
	K=3	L=-6			0	3	10	-93	-152
1	3	-6	161	229					
3	3	-6	-149	-154		K=3	L=11		
4	3	-6	157	155	1	3	11	546	510
5	3	-6	92	107	2	3	11	-147	-146

TABLE A3.14

F(OBS), F(CALC) FOR $[\text{VCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ (UNOBSERVED REFLECTIONS MARKED*)

H	K	L	F _O	K*F _L	H	K	L	F _O	K*F _L
K= 0, L= 0					K= 2, L= 2				
1	0	0	311	266	1	2	2	-26	-47
2	0	0	-154	-63	-3	2	2	149	167
3	0	0	100	66	-3	2	2	-96	-95
K= 0, L= 2					-1	2	2	397	420
-3	0	2	133	116	1	2	2	-454	-473
-3	0	2	-255	-244	3	2	2	237	216
-2	0	2	447	412	K= 2, L= 3				
-1	0	2	413	420	-3	2	3	-143	-127
1	0	2	-64	-79	-1	2	3	150	146
2	0	2	765	767	K= 2, L= 4				
3	0	2	344	267	-3	2	4	203	236
0	0	2	222	231	-1	2	4	-36	-167
K= 0, L= 4					1	2	4	246	306
-3	0	4	166	177	3	2	4	-294	-247
-3	0	4	233	165	K= 2, L= 5				
-2	0	4	314	364	-1	2	5	-79	-71
-1	0	4	-457	-465	1	2	5	116	125
1	0	4	491	513	K= 2, L= 6				
2	0	4	585	594	-3	2	6	119	117
3	0	4	-135	-97	-1	2	6	127	141
0	0	4	158	136	K= 2, L= 8				
K= 0, L= 6					-1	2	8	146	162
-3	0	6	138	136	3	2	8	137	104
-3	0	6	-122	-72	K= 3, L= 0				
-2	0	6	135	130	3	3	0	-161	-139
1	0	6	-91	-64	K= 3, L= 1				
2	0	6	101	75	-3	3	1	131	120
3	0	6	145	156	-3	3	1	298	242
0	0	6	-97	-20	-1	3	1	369	377
K= 0, L= 8					1	3	1	171	161
-3	0	8	99	72	3	3	1	434	375
-3	0	8	-93	-65	K= 3, L= 2				
-2	0	8	209	237	-1	3	2	147	161
-1	0	8	143	121	K= 3, L= 3				
1	0	8	-166	-164	-3	3	3	210	235
2	0	8	230	213	-3	3	3	105	49
3	0	8	167	115	-1	3	3	395	469
K= 0, L= 10					1	3	3	194	169
-2	0	10	193	242	3	3	3	242	211
-1	0	10	98	25	0	3	3	168	194
2	0	10	141	127	K= 3, L= 4				
K= 1, L= 0					-1	3	4	123	117
3	1	0	125	65	K= 3, L= 5				
0	1	0	95	57	-3	3	5	311	278
K= 1, L= 1					-1	3	5	83	107
-3	1	1	224	220	1	3	5	346	348
-3	1	1	268	243	3	3	5	106	98
-1	1	1	510	513	0	3	5	124	172
1	1	1	393	312	K= 3, L= 6				
3	1	1	448	367	1	3	6	132	137
0	1	1	136	101	K= 3, L= 7				
K= 1, L= 2					-3	3	7	163	140
-3	1	2	-189	-160	-1	3	7	166	196
-1	1	2	-72	-33	1	3	7	171	182
1	1	2	-107	-94	3	3	7	169	161
K= 1, L= 3					K= 4, L= 0				
-3	1	3	347	314	1	4	0	72	77
-3	1	3	139	131	3	4	0	104	62
-1	1	3	476	503	K= 4, L= 1				
1	1	3	355	353	-1	4	1	-125	-132
3	1	3	228	203	1	4	1	72	64
0	1	3	223	209	K= 4, L= 2				
K= 1, L= 4					-3	4	2	-117	-99
-1	1	4	-129	-112	-1	4	2	217	243
K= 1, L= 5					1	4	2	-105	-107
-3	1	5	478	510	3	4	2	210	192
1	1	5	395	468	K= 4, L= 3				
3	1	5	123	154	1	4	3	-112	-117
0	1	5	139	153	3	4	3	61	69
K= 1, L= 6					K= 4, L= 4				
-3	1	6	139	105	-1	4	4	-63	-64
K= 1, L= 7					K= 1, L= 8				
-3	1	7	161	178	-3	1	8	94	87
-1	1	7	286	354	K= 1, L= 9				
1	1	7	139	132	-1	1	9	319	334
3	1	7	229	253	3	1	9	164	180
K= 1, L= 8					K= 2, L= 0				
-3	1	8	94	87	1	2	0	-141	-104
K= 1, L= 9					3	2	0	121	95
-1	1	9	319	334	K= 2, L= 1				
3	1	9	164	180	-1	2	1	153	91
K= 2, L= 0					K= 2, L= 1				
1	2	0	-141	-104	K= 2, L= 1				
3	2	0	121	95	K= 2, L= 1				
K= 2, L= 1					K= 2, L= 1				
-1	2	1	153	91	K= 2, L= 1				

Appendix 4Literature Review V(III) Structures

Detailed surveys of the structural chemistry of transition metal compounds have been carried out up to 1968 by Colton and Canterford¹⁰³, by Nichols¹⁰⁴, and on V(III) in particular by Clark¹⁰⁵. Podmore⁶¹ has continued the survey of halides and oxy-halides of first row transition elements to September 1972.

A summary of the structural data obtained from powder and single crystal X-ray diffraction studies on compounds of vanadium(III), is presented here in tabular form.

TABLE A.4.1

Reported structural data for halides, oxy-halides and
some related compounds of vanadium(III)

Compound	Cell dimensions	Comments	References
VF_3	$a = 5.373 \text{ \AA}$ $\alpha = 57.9^\circ$	Rhombohedral $\text{V-F} = 1.95 \text{ \AA}$	106
VCl_3	$a = 6.735 \text{ \AA}$ $\alpha = 53.0^\circ$	Rhombohedral $\text{V-Cl} = 2.46 \text{ \AA}$	98
	$a = 6.012 \text{ \AA}$ $c = 17.34 \text{ \AA}$	Hexagonal	98
	$a = 6.045 \text{ \AA}$ $c = 17.45 \text{ \AA}$	Hexagonal	107
VBr_3	$a = 6.40 \text{ \AA}$ $c = 18.53 \text{ \AA}$	Hexagonal	6
VI_3	$a = 6.919 \text{ \AA}$ $c = 19.91 \text{ \AA}$	Hexagonal	109
			110
VOF		Tetragonal	105
VOCl	$a = 3.78 \text{ \AA}$ $b = 3.30 \text{ \AA}$ $c = 7.91 \text{ \AA}$	Orthorhombic	111(112,113)
CsNiVF_6 CsCuVF_6 CsCoVF_6 CsFeVF_6 CsMnVF_6	$a = 10.36 \text{ \AA}$ $a = 10.39 \text{ \AA}$ $a = 10.42 \text{ \AA}$ $a = 10.48 \text{ \AA}$ $a = 10.57 \text{ \AA}$	Cubic	114
K_3VF_6	$a = 8.70 \text{ \AA}$	Cubic	115(116)

TABLE A.4.1 (Cont.)

$(\text{NH}_4)_3\text{VF}_6$ Rb_3VF_6 Tl_3VF_6 Cs_3VF_6	$a = 9.04 \text{ \AA}$ $a = 9.07 \text{ \AA}$ $a = 9.04 \text{ \AA}$ $a = 9.47 \text{ \AA}$	Cubic	117,118 119 115 115
$(\text{NH}_4)_2\text{VF}_5 \cdot \text{H}_2\text{O}$ $\text{Rb}_2\text{VF}_5 \cdot \text{H}_2\text{O}$ $\text{Tl}_2\text{VF}_5 \cdot \text{H}_2\text{O}$	$a = 8.42 \text{ \AA}$ $a = 8.42 \text{ \AA}$ $a = 8.45 \text{ \AA}$	Cubic	120
KVF_4	$a = 7.596 \text{ \AA}$ $b = 7.738 \text{ \AA}$ $c = 12.28 \text{ \AA}$	Orthorhombic	121
RbVF_4	$a = 7.596 \text{ \AA}$ $c = 6.315 \text{ \AA}$ $a = 3.78 \text{ \AA}$ $c = 6.23 \text{ \AA}$ $a = 8.34 \text{ \AA}$	Tetragonal Tetragonal Cubic above 500°C	121 122 122
$\text{Cs}_3\text{V}_2\text{Cl}_9$	$a = 7.24 \text{ \AA}$ $c = 17.94 \text{ \AA}$	Hexagonal Isomorphous with $\text{Cs}_3\text{Cr}_2\text{Cl}_9$	123
V_2O_3	$a = 5.647 \text{ \AA}$ $\alpha = 53^\circ 45'$	$\text{V-O} = 1.96 \text{ \AA}$ and 2.06 \AA Rhombohedral	124

TABLE A.4.2

Reported Crystallographic data for complexes of vanadium(III)

	$K_3[V(C_2O_4)_3]^{90,91}$	$VCl_3(NMe_3)_2^{92}$	$V[PS_2(OEt)_2]_3^{93}$	$[(\pi-C_5H_5)V(CF_3COO)_2]_2^{94}$
a(Å)	7.81	9.817	8.644	9.00
b(Å)	20.01	10.127	18.487	8.75
c(Å)	10.35	13.152	17.688	8.88
$\alpha(^{\circ})$				65.90°
β	108.6°		93°	105.5°
γ				102.8°
z	4	4	4	1
d_{calc}	2.102 g/cc	1.4 g/cc	1.43 g/cc	1.81 g/cc
d_{obs}	2.09 g/cc			1.78 g/cc
Space Group	$P2_1/c$	Pnma	C2/c	P1
Observed	1350	573	1124	750
Reflections				
Final R.	.15	.074	.077	.14
V-Cl(Av)	No bond lengths given	2.239		
V-O(bridge)				2.05 Å